NEW DIFFRACTION DATA

Powder X-ray diffraction structural characterization of the coordination complex *cis*-[Co($\kappa^2 N,N'$-1,10-phenanthroline-5,6-dione)$_2$Cl$_2$]

José A. Fernandes,[1] Olufunso Abosede,[2] and Simona Galli[1,a)]

[1]*Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy*
[2]*Department of Chemistry, Federal University Otuoke, PMB 126, Yenagoa, Bayelsa State, Nigeria*

The reduction of *cis*-[Co^{III}($\kappa^2 N,N'$-1,10-phenanthroline-5,6-dione)$_2$Cl$_2$]Cl into the neutral compound *cis*-[Co^{II}($\kappa^2 N,N'$-1,10-phenanthroline-5,6-dione)$_2$Cl$_2$] was observed during developmental studies of new antimalarial drugs. The crystal structure of *cis*-[Co^{II}($\kappa^2 N,N'$-1,10-phenanthroline-5,6-dione)$_2$Cl$_2$] was unveiled by powder X-ray diffraction studies (PXRD). PXRD details, unit cell parameters, and space group for *cis*-[Co^{II}($\kappa^2 N,N'$-1,10-phenanthroline-5,6-dione)$_2$Cl$_2$], C$_{24}$H$_{12}$Cl$_2$CoN$_4$O$_4$, are reported [$a = 41.4951$ (13) Å, $b = 8.2768$ (2) Å, $c = 12.4994$ (3) Å, unit cell volume $V = 4292.9$ (2) Å^3, $Z = 8$, and space group $Fdd2$]. Infrared spectroscopy features are also discussed. © *2018 International Centre for Diffraction Data*. [doi:10.1017/S0885715618000143]

I. INTRODUCTION

Malaria is a disease provoked by *Plasmodium* parasites and is spread by mosquitoes of the genus *Anopheles* (WHO, 2016). Chloroquine (Scheme 1) is an active pharmaceutical ingredient recommended by the World Health Organization for the treatment of malaria and rheumatoid disorders (WHO, 2015). However, the efficacy of this drug has been diminishing because of the emergence of chloroquine-resistant malaria parasites (Navarro *et al.*, 2014). For this reason, studies aiming at individuating new effective drugs against malaria are of extreme importance. One research line in this context is focused on coordination compounds containing chloroquine as ligand. Several complexes of chloroquine and its derivatives are known (Biot *et al.*, 2012; Salas *et al.*, 2013). Among them, some complexes of ruthenium (Sánchez-Delgado *et al.*, 1996; Rajapakse *et al.*, 2009), iridium (Navarro *et al.*, 2007), platinum (Navarro *et al.*, 2014), and gold (Navarro *et al.*, 1997, 2004, 2014) have shown enhanced antimalarial activity in comparison to chloroquine.

Phendione (1,10-phenanthroline-5,6-dione, Scheme 1) is a versatile chelating ligand with excellent ability to form stable coordination complexes with a wide variety of metal ions (Goss and Abruna, 1985; Brechin *et al.*, 2008). It possesses two coordination moieties, namely orthoquinone, which is redox reactive, and *α*-diimine, which imparts Lewis-basicity. It has been recently demonstrated that the coordination of phendione to transition metal ions improves its biological activity (Roy *et al.*, 2008; Chang *et al.*, 2010; Viganor *et al.*, 2015). Indeed, phendione has been widely used in the preparation of mono-, bi-, and poly(nuclear) complexes (Paw and Eisenberg, 1997; Calderazzo *et al.*, 1999; Brechin *et al.*, 2008) and their potential applications as redox agents have been studied (Fujihara *et al.*, 2003). Studies on their anti-microbial or cytotoxic effects (McCann *et al.*, 2004; Silva

et al., 2013) and interaction with DNA have also been carried out (Roy *et al.*, 2008; Poteet *et al.*, 2013). Overall, the functional properties of these complexes are modulated by the distribution of the electronic density, which is dictated by the oxidation state of the metal ion and phendione.

In our efforts to synthesize ternary cobalt complexes with phendione and chloroquine in order to obtain compounds with possible applications as therapeutic agents, we serendipitously isolated *cis*-[Co^{II}($\kappa^2 N,N'-$1,10-phenanthroline-5,6-dione)$_2$ Cl$_2$] in the form of microcrystalline powders from the reduction of *cis*-[Co^{III}($\kappa^2 N,N'-$1,10-phenanthroline-5,6-dione)$_2$ Cl$_2$]Cl in the reaction medium. In this study, the crystal structure of *cis*-[Co^{II}($\kappa^2 N,N'-$1,10-phenanthroline-5,6-dione)$_2$Cl$_2$], *cis*-[Co(phendione)$_2$Cl$_2$], was investigated by means of laboratory powder X-ray diffraction (PXRD).

II. EXPERIMENTAL

A. Materials and methods

All chemicals used for the syntheses were of analytical grade and were used as received. Chloroquine diphosphate was obtained from Sam pharmaceuticals Plc, Ilorin, Nigeria. Phendione and *cis*-[Co^{III}($\kappa^2 N,N'-$1,10-phenanthroline-5,6-dione)$_2$Cl$_2$]Cl, *cis*-[Co(phendione)$_2$Cl$_2$]Cl, were synthesized by applying slight modifications to previously reported procedures (Vlcek, 1967; Yamada *et al.*, 1992; Ghosh *et al.*, 2006). Infrared spectra were recorded on a Perkin Elmer 400 ATR-FTIR spectrometer on powdered samples pressed as KBr pellets. Elemental analyses were carried out with an Elementar Analysen systeme Vario ® MICRO VI 6.2 GmbH instrument.

B. Synthesis of *cis*-[Co(phendione)$_2$Cl$_2$]

Chloroquine diphosphate (128 mg, 0.248 mmol), *cis*-[Co (phendione)$_2$Cl$_2$]Cl (146 mg, 0.249 mmol) and trimethylamine (0.1 ml) were refluxed in water:methanol (1 : 1, 15 ml) for about 3 h. The resulting orange solution was filtered
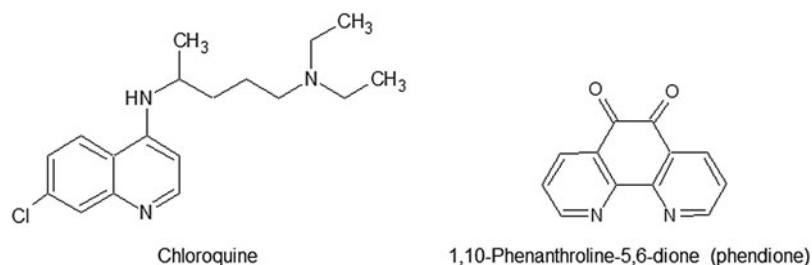
Scheme 1. Molecular structure of chloroquine (left) and 1,10-phenanthroline-5,6-dione (right).

and allowed to evaporate slowly at room temperature. An orange precipitate formed after 1 week, which was collected by filtration, and dried in a desiccator. Yield: 96 mg, 70%. Analytical data for $C_{24}H_{12}Cl_2CoN_4O_4$: MW 550.21 g mol^{-1}; Wt% exp (calc): %C, 52.24 (52.39); %H, 1.67 (2.20); %N, 9.67 (10.18).

C. PXRD structural characterization

A powdered sample of *cis*-[Co(phendione)$_2$Cl$_2$], gently ground with agate mortar and pestle, was deposited in the hollow of a silicon zero-background plate 0.2 mm deep (supplied by Assing Srl, Monterotondo, Italy). Data acquisitions were performed on a vertical-scan Bruker AXS D8 Advance θ:θ diffractometer, equipped with a Bruker Lynxeye linear position-sensitive detector, primary beam Sollers slits (2.5°), divergence slit (1 mm), antiscatter slit (20 mm), and Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å). The generator was set at 40 kV and 40 mA. After a preliminary acquisition for finger printing analysis in the 3–35° 2θ range, diffraction data for a full structure determination were collected up to 105° 2θ, with steps of 0.02°, with an overall scan time of approximately 16 h. A standard peak search, followed by profile fitting, enabled us to estimate the low-to-medium angle peak maximum positions. Approximate unit cell parameters were obtained through the singular value decomposition algorithm (Coelho, 2003) implemented in TOPAS Academic 4.1

(Coelho, 2007). A search in the Cambridge Structural Database v. 1.18 (Groom *et al.*, 2016) revealed the existence of two compounds with similar content, space group, and unit cell, namely: *cis*-[Hg(phendione)$_2$Cl$_2$] (Figueiras *et al.*, 2009; Ma *et al.*, 2010) and *cis*-[Cu(phendione)$_2$Br$_2$] (Stephenson and Hardie, 2006). A trial Rietveld refinement with a model in Cartesian coordinates extracted from the latter crystal structure gave a reasonable fit to our experimental data. This result suggested to us that the two compounds are isostructural. This evidence was further confirmed by performing an independent structure determination adopting a combined Monte Carlo/simulated annealing approach, as implemented in TOPAS Academic 4.1 (Coelho, 2007), where phendione was described as a rigid body (expressed in Cartesian coordinates, extracted from the crystal structure of Stephenson and Hardie, 2006). The position of its centre of mass and its orientation within the unit cell were allowed to vary, along with the positions of the Cl and Co atoms. Structure refinement was carried out by the Rietveld method (Young, 1981), maintaining the rigid body used at the structure solution stage. The background was modelled using a polynomial function of the Chebyshev type, while peak profiles were described by the Fundamental Parameters Approach (Cheary and Coelho, 1992). A common, refined isotropic thermal factor B_{iso} (C, H, N, O) was attributed to all atoms except Cl and Co, to which the isotropic thermal factor $B_{iso}(Cl, Co) = B_{iso}(C,H,N, O) - 2.0$ Å^2 was assigned. A correction for preferred
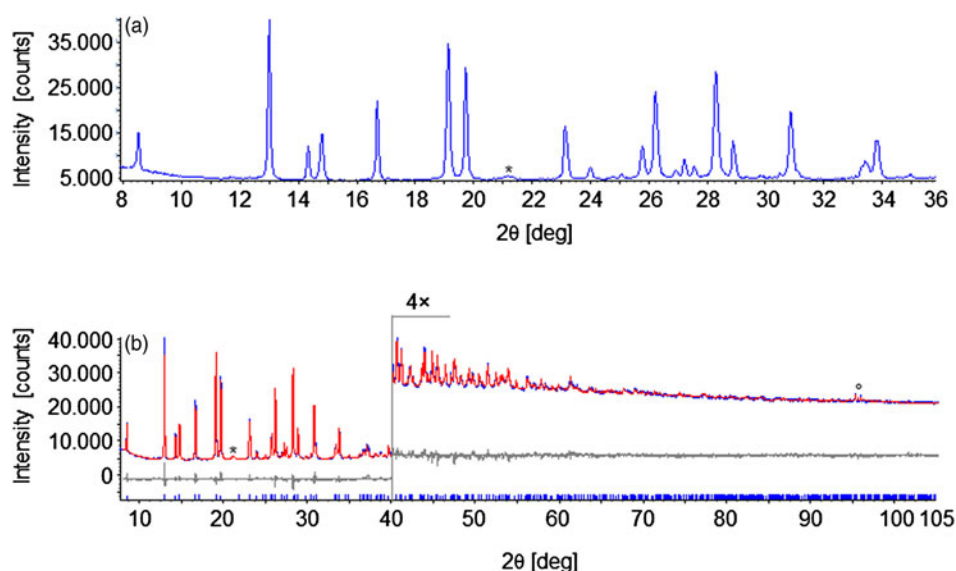
Figure 1. (Colour online) (a) Low-to-medium angle portion of the PXRD pattern of *cis*-[Co(phendione)$_2$Cl$_2$]. (b) Graphical result of the final Rietveld refinement carried out on *cis*-[Co(phendione)$_2$Cl$_2$], in terms of experimental, calculated, and difference traces (blue, red and grey, respectively). The blue markers at the bottom indicate the positions of the Bragg reflections. Horizontal axis, 2θ [deg]; vertical axis, intensity [counts]. The portion above 40° has been magnified. The asterisk in (a) and (b) marks a peak belonging to an impurity, while the circle in (B) marks peaks belonging to the Si zero-background sample holder.

TABLE I. Powder X-ray diffraction data for *cis*-[Co(phendione)$_2$Cl$_2$] (Cu$K\alpha_1$ component, $\lambda = 1.5406$ Å).

$2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	$\Delta2\theta$
8.510	10.381	43	4	0	0	8.513	10.378	0.003
12.987	6.811	100	1	1	1	12.988	6.811	0.001
14.324	6.179	22	3	1	1	14.325	6.178	0.001
14.784	5.987	35	2	0	2	14.784	5.987	−0.001
16.684	5.309	46	5	1	1	16.687	5.309	0.003
17.068	5.191	1	8	0	0	17.074	5.189	0.006
19.114	4.640	89	6	0	2	19.116	4.639	0.002
19.714	4.500	70	7	1	1	19.719	4.499	0.004
21.870	4.061	1	2	2	0	21.872	4.060	0.002
23.107	3.846	29	4	2	0	23.110	3.846	0.003
23.167	3.836	13	9	1	1	23.173	3.835	0.006
23.977	3.708	9	1	1	3	23.976	3.709	−0.001
24.742	3.596	2	3	1	3	24.741	3.596	0.000
25.040	3.553	3	6	2	0	25.044	3.553	0.004
25.723	3.460	10	12	0	0	25.732	3.459	0.009
25.733	3.459	7	10	0	2	25.739	3.458	0.006
25.785	3.452	11	0	2	2	25.786	3.452	0.001
26.146	3.406	7	2	2	2	26.147	3.405	0.001
26.208	3.398	64	5	1	3	26.209	3.397	0.001
26.895	3.312	6	11	1	1	26.903	3.311	0.007
27.200	3.276	14	4	2	2	27.202	3.276	0.002
27.534	3.237	9	8	2	0	27.539	3.236	0.005
28.276	3.154	89	7	1	3	28.278	3.153	0.002
28.528	3.126	2	0	0	4	28.526	3.127	−0.002
28.877	3.089	27	6	2	2	28.880	3.089	0.003
29.822	2.994	2	4	0	4	29.821	2.994	−0.001
30.462	2.932	2	10	2	0	30.469	2.931	0.007
30.818	2.899	12	13	1	1	30.827	2.898	0.009
30.834	2.898	47	9	1	3	30.838	2.897	0.003
31.087	2.875	3	8	2	2	31.091	2.874	0.004
33.281	2.690	8	1	3	1	33.284	2.690	0.003
33.409	2.680	4	14	0	2	33.418	2.679	0.009
33.432	2.678	7	8	0	4	33.434	2.678	0.001
33.728	2.655	3	12	2	0	33.736	2.655	0.008
33.735	2.655	9	10	2	2	33.741	2.654	0.006
33.785	2.651	20	11	1	3	33.790	2.651	0.005
33.852	2.646	7	3	3	1	33.855	2.646	0.003
34.889	2.570	1	15	1	1	34.900	2.569	0.011
34.968	2.564	1	5	3	1	34.972	2.564	0.004
36.234	2.477	4	2	2	4	36.233	2.477	−0.001
36.587	2.454	8	7	3	1	36.592	2.454	0.005
36.743	2.444	8	12	2	2	36.750	2.444	0.007
37.027	2.426	7	4	2	4	37.027	2.426	0.000
37.052	2.424	10	13	1	3	37.058	2.424	0.007
37.260	2.411	14	14	2	0	37.270	2.411	0.010
38.114	2.359	3	3	1	5	38.112	2.359	−0.002
38.317	2.347	3	6	2	4	38.318	2.347	0.001
38.654	2.327	5	9	3	1	38.660	2.327	0.006
38.787	2.320	5	12	0	4	38.791	2.320	0.005
39.170	2.298	2	1	3	3	39.171	2.298	0.002
39.666	2.270	14	3	3	3	39.668	2.270	0.002
40.045	2.250	3	14	2	2	40.053	2.249	0.009
40.064	2.249	8	8	2	4	40.067	2.249	0.002
40.575	2.222	11	15	1	3	40.584	2.221	0.009
40.645	2.218	11	5	3	3	40.647	2.218	0.003
41.009	2.199	3	16	2	0	41.021	2.199	0.011
41.114	2.194	14	11	3	1	41.121	2.193	0.007
41.697	2.164	1	18	0	2	41.710	2.164	0.013
42.077	2.146	7	7	3	3	42.080	2.146	0.003
42.222	2.139	6	10	2	4	42.226	2.139	0.004
42.503	2.125	5	9	1	5	42.505	2.125	0.001
43.392	2.084	2	19	1	1	43.406	2.083	0.014
43.554	2.076	3	20	0	0	43.570	2.076	0.015
43.593	2.075	1	16	2	2	43.604	2.074	0.011
43.610	2.074	4	2	0	6	43.606	2.074	−0.003
43.686	2.070	3	0	4	0	43.690	2.070	0.004
43.914	2.060	2	2	4	0	43.918	2.060	0.004
43.915	2.060	2	13	3	1	43.924	2.060	0.009
43.927	2.060	12	9	3	3	43.932	2.059	0.005
44.315	2.042	3	17	1	3	44.326	2.042	0.010
44.592	2.030	1	4	4	0	44.596	2.030	0.005
44.743	2.024	5	12	2	4	44.748	2.024	0.005
44.789	2.022	7	11	1	5	44.791	2.022	0.003
44.943	2.015	5	18	2	0	44.956	2.015	0.013
45.380	1.997	6	16	0	4	45.388	1.997	0.008
45.410	1.996	5	6	0	6	45.408	1.996	−0.002
45.704	1.984	3	6	4	0	45.709	1.983	0.005
46.156	1.965	2	11	3	3	46.162	1.965	0.006
46.367	1.957	8	2	4	2	46.371	1.957	0.004
47.013	1.931	2	15	3	1	47.023	1.931	0.010
47.018	1.931	3	4	4	2	47.022	1.931	0.004
47.355	1.918	5	18	2	2	47.367	1.918	0.012
47.416	1.916	5	13	1	5	47.420	1.916	0.004
47.586	1.909	6	14	2	4	47.593	1.909	0.007
47.808	1.901	1	21	1	1	47.824	1.900	0.016
48.086	1.891	3	6	4	2	48.091	1.890	0.005
48.244	1.885	4	19	1	3	48.256	1.884	0.012
48.883	1.862	1	0	2	6	48.881	1.862	−0.002
49.042	1.856	2	20	2	0	49.057	1.855	0.015
49.092	1.854	2	2	2	6	49.090	1.854	−0.002
49.132	1.853	1	10	4	0	49.139	1.853	0.007
49.167	1.852	4	1	3	5	49.167	1.852	0.000
49.553	1.838	2	8	4	2	49.559	1.838	0.006
49.582	1.837	5	3	3	5	49.583	1.837	0.000
49.716	1.832	2	4	2	6	49.714	1.832	−0.001
50.347	1.811	2	15	1	5	50.353	1.811	0.006
50.406	1.809	2	5	3	5	50.407	1.809	0.001
50.464	1.807	1	22	0	2	50.481	1.806	0.016
51.307	1.779	4	20	2	2	51.321	1.779	0.014
51.388	1.777	2	12	4	0	51.397	1.776	0.009
51.394	1.776	6	10	4	2	51.401	1.776	0.007
51.602	1.770	1	15	3	3	51.611	1.770	0.009
52.153	1.752	1	8	2	6	52.154	1.752	0.000
52.335	1.747	2	23	1	1	52.352	1.746	0.018
52.345	1.746	1	21	1	3	52.360	1.746	0.014
52.399	1.745	3	1	1	7	52.395	1.745	−0.004
52.796	1.733	1	3	1	7	52.792	1.733	−0.003
52.872	1.730	1	24	0	0	52.891	1.730	0.019
52.893	1.730	2	20	0	4	52.905	1.729	0.012
53.007	1.726	4	0	4	4	53.009	1.726	0.002
53.204	1.720	1	2	4	4	53.206	1.720	0.002
53.216	1.720	1	9	3	5	53.218	1.720	0.003
53.295	1.718	2	22	2	0	53.312	1.717	0.017
53.584	1.709	1	5	1	7	53.581	1.709	−0.003
53.581	1.709	1	12	4	2	53.589	1.709	0.008
53.706	1.705	2	14	0	6	53.710	1.705	0.004
53.793	1.703	5	4	4	4	53.795	1.703	0.003
53.930	1.699	1	10	2	6	53.931	1.699	0.001
53.967	1.698	1	14	4	0	53.977	1.697	0.010
53.968	1.698	1	19	3	1	53.982	1.697	0.014
54.099	1.694	1	18	2	4	54.109	1.694	0.010
54.751	1.675	1	7	1	7	54.749	1.675	−0.002
54.755	1.675	1	17	3	3	54.765	1.675	0.011
54.764	1.675	1	6	4	4	54.767	1.675	0.003
56.005	1.641	1	1	5	1	56.010	1.641	0.005
56.048	1.639	1	12	2	6	56.051	1.639	0.003
56.090	1.638	1	14	4	2	56.099	1.638	0.009
56.105	1.638	3	8	4	4	56.109	1.638	0.004
56.282	1.633	1	9	1	7	56.281	1.633	−0.001
56.384	1.631	2	3	5	1	56.390	1.630	0.006
56.610	1.625	1	23	1	3	56.626	1.624	0.016

Continued

TABLE I. Continued

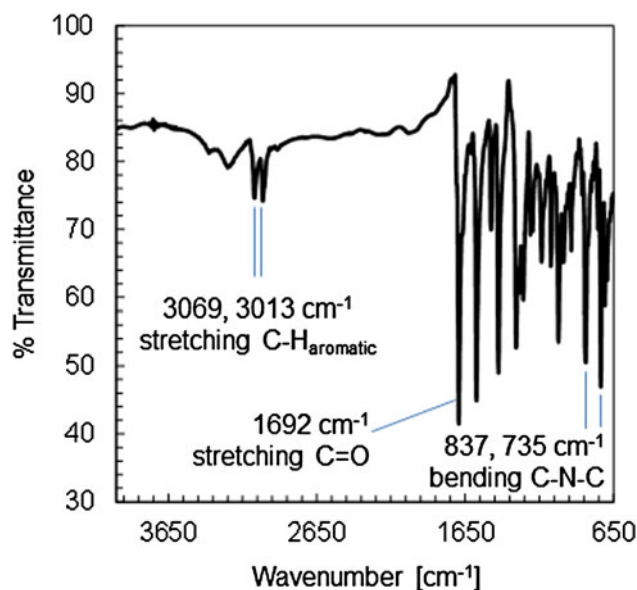| $2\theta_{obs}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{cal}$	d_{cal}	$\Delta 2\theta$
56.841	1.618	2	16	4	0	56.853	1.618	0.012
56.976	1.615	1	25	1	1	56.996	1.614	0.020
57.436	1.603	1	13	3	5	57.441	1.603	0.005

orientation was applied, adopting the March–Dollase model (March, 1932; Dollase, 1986), along the [111] direction. The raw data and the final Rietveld refinement plot are shown in Figure 1. The pertinent CIF file is supplied as electronic Supplementary Information. Table I provides a reflection list for the low-to-medium angle PXRD pattern. The main crystal data and refinement parameters are reported in Table II. CCDC 1533381.

III. DISCUSSION

The compound cis-[Co(phendione)$_2$Cl$_2$] was serendipitously obtained during our attempts to synthesize ternary cobalt complexes of phendione with the biologically relevant ligand chloroquine. More in detail, the reaction of cis-[Co(phendione)$_2$Cl$_2$]Cl and chloroquine diphosphate in water–methanol (1:1, v/v) and in the presence of triethylamine, yielded an orange precipitate. Its elemental analysis purported the formation of the coordination complex cis-[Co(phendione)$_2$Cl$_2$], suggesting the reduction of Co(III) to Co(II) in the reaction medium. Rather recently, the hydrated form cis-[Co(phendione)$_2$Cl$_2$]·H$_2$O was isolated by reacting CoCl$_2$·6H$_2$O and phendione in ethanol, and tested as anti-Candida agent (Cogan, 2009). Nonetheless, no crystal structure determination has been carried out on the hydrated form. The IR spectrum of cis-[Co(phendione)$_2$Cl$_2$] (Figure 2) exhibits bands at 3069 and 3013 cm^{-1} because of the stretching of the aromatic C–H bonds of phendione. The strong-intensity band at 1692 cm^{-1} is because of the stretching of the C=O bond of phendione, while the bands at 837 and 735 cm^{-1} are because of the C–N–C bending vibrations. These values are in fair agreement with those of phendione (3434–3066, 1685, 806, and 735 cm^{-1}, respectively), and

TABLE II. Crystal data and refinement parameters for cis-[Co(phendione)$_2$Cl$_2$].

Parameter	Data
Formula	C$_{24}$H$_{12}$Cl$_2$CoN$_4$O$_4$
fw (g mol^{-1})	550.21
System	Orthorhombic
Space group	Fdd2
a (Å)	41.4951 (13)
b (Å)	8.2768 (2)
c (Å)	12.4994 (3)
V (Å^3)	4292.9 (2)
Z	8
$F(000)$	2216
ρ (g cm^{-3})	1.703
2θ range	8–105°
Data, parameters	4851, 39
R_p, R_{wp}	0.024, 0.033
R_{Bragg}	0.016

Figure 2. (Colour online) Infrared spectrum of cis-[Co(phendione)$_2$Cl$_2$] with assignation of the main bands.

those (3070–3000, 1694, 839, and 730 cm^{-1}, respectively) reported by Cogan (2009) for cis-[Co(phendione)$_2$Cl$_2$]·H$_2$O.

Kawade et al. (2010) have recently investigated the reduction of cis-[Co(phendione)$_2$Cl$_2$]Cl by a number of radical species, among which the dimethylketyl [E$_0$ = −1.4 V vs. normal hydrogen electrode (NHE)] and carbon dioxide (E$_0$ = −1.9 V vs. NHE) radicals. In all of the cases, the first step of the reduction involves the phendione ligand, which then transfers the electron to the metal centre. Then, the complex may suffer ligand loss or solvation. In this respect, a radical scavenger as benzophenone could successfully act as complex protector. Mammo and Shanshal (1977) determined $E_{1/2}$ values of −1.32 and −1.80 V [vs. saturated calomel electrode (SCE)] for chloroquine, which translate into E_0 potentials approximately equal to −1.08 and −1.60 V, respectively (indeed, excluding diffusion, $E_{NHE} = E_{SCE} + 0.241$ V). Since the second standard reduction potential of chloroquine is lower than the standard reduction potential of the dimethylketyl radical, it is plausible that chloroquine can reduce cis-[Co(phendione)$_2$Cl$_2$]Cl to the title compound in the essayed reaction conditions.

The crystal and molecular structure of cis-[Co(phendione)$_2$Cl$_2$] was unravelled by a PXRD study, using cis-[Cu(phendione)$_2$Br$_2$] as a model for a preliminary assessment (Stephenson and Hardie, 2006) (see Experimental section for further details).

The main crystal data and data analysis parameters for cis-[Co(phendione)$_2$Cl$_2$] are reported in Table II, while Table III contains relevant fractional coordinates and geometrical parameters. cis-[Co(phendione)$_2$Cl$_2$] crystallizes in the orthorhombic space group Fdd2. Its asymmetric unit comprises one cobalt(II) ion, located on a two-fold axis, one phendione molecule and one charge-balancing chloro ligand. The metal centres show a slightly distorted octahedral coordination geometry defined by two chelating phendione ligands and two chloro ligands [Figure 3(a)]. The latter are in cis disposition at a distance Co–Cl1 of 2.427 (5) Å [see Figure 3(a) for the labels], and an angle Cl1–Co–Cl1^i of 93.0 (3)° (symmetry operation i: ½−x, ½−y, z). The nitrogen atoms of phendione show Co–N1 and Co–N2 distances of 2.09 (2) and 2.16 (3) Å,

TABLE III. Relevant fractional atomic coordinates and geometrical parameters for *cis*-[Co(phendione)$_2$Cl$_2$].

Atom	Site	x/a	y/b	z/c
Co	2	¼	¼	0.1994 (5)
Cl1	1	0.21789 (11)	0.1112 (6)	0.06567
N1	1	0.28103	1.32903	0.31995
N2	1	0.28128	1.04440	0.22481

Atoms	Distances (Å)		Atoms	Angles (degrees)
Co–Cl1	2.427 (5)		Cl1–Co–N1	90.6 (9)
Co–N1	2.09 (2)		Cl1–Co–N2	98.3 (8)
Co–N2	2.16 (3)		N1–Co–N2	76.7 (8)
Supramolecular interactions			Cl1–Co–Cl1^{ii}	93.0 (3)
Cl1···Cg^i	3.6275		Cl1–Co–N1^{ii}	169.8 (10)
Cg = centroid of {C4, C5, C9–C12}			Cl1–Co–N2^{ii}	93.3 (7)
			N1–Co–N1^{ii}	87.6 (17)
Symmetry operations			N1–Co–N2^{ii}	91.0 (13)
i) x, ½ + y, −½ + z; ii) ½−x, ½−y, z			N2–Co–N2^{ii}	163.1 (14)

respectively, and a bite angle of 76.7 (8)°. The remaining *cis* angles of the octahedron range in the interval 90.6 (9)–98.3 (8)°, while the *trans* angles of the octahedron are 163.1 (14) and 169.8 (10)°.

A survey within the Cambridge Structural Database v. 1.18 (Groom *et al.*, 2016) revealed that for mononuclear compounds containing the fragment *cis*-Co(II)(halo)$_2$(κ^2N, N')$_2$ (where κ^2N,N' represents 2,2′-bipyridine or 1,10-phenanthroline derivatives), the values of the Co–N distance fall in the range 2.11–2.21 Å (11 compounds, with 32 crystallographically independent Co–N bonds). For compounds of the type *cis*-Co(II)(chloro)$_2$(κ^2N,N')$_2$ the values of the Co–Cl distance fall in the range 2.37–2.45 Å (eight compounds, with 14 crystallographically independent Co–Cl bonds). This means that, in [Co(phendione)$_2$Cl$_2$], the distances between the metal centre and the first coordination sphere are inside or very near known ranges. A charge value of +1.9 for the metal centre, as calculated by the bond valence parameters (Brown and Altermatt, 1985), is in close agreement with the expected value of +2. Because of the distance of the complexes within the herring-bone packing [Figure 3 (b)], no strong supramolecular interactions are found in this crystal structure. Among the weak supramolecular interactions, a Cl1···π (Cl1···Cg 3.6275 Å, Cg = centroid of {C4, C5, C9–C12}) interaction is noteworthy.

As anticipated in the Experimental section, to the best of our knowledge, two isotypic compounds, *cis*-[Hg (phendione)$_2$Cl$_2$] (Figueiras *et al.*, 2009; Ma *et al.*, 2010)
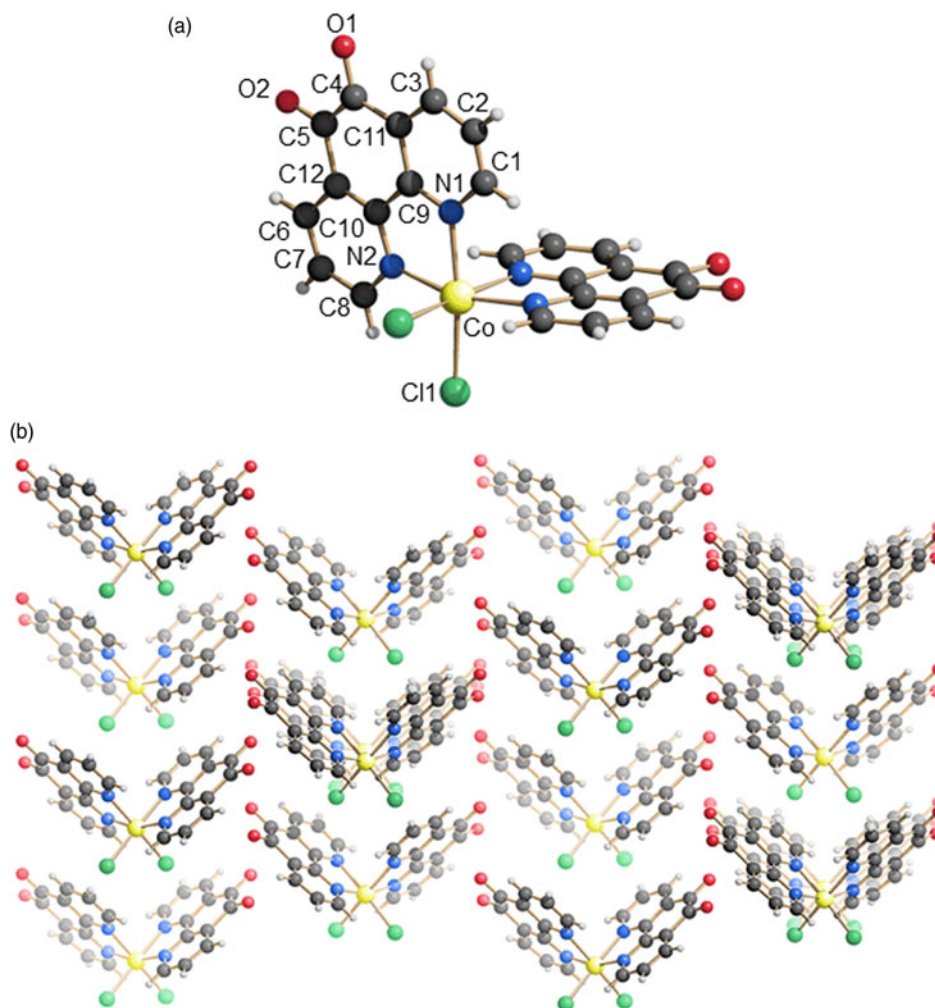

Figure 3. (Colour online) Representation of the crystal structure of *cis*-[Co(phendione)$_2$Cl$_2$]. (a): the complex, with the labels adopted throughout the manuscript. (b) Portion of the packing viewed in perspective along the *b*-axis. Horizontal axis, *c*; vertical axis, *a*. Carbon, grey; hydrogen, light grey; chlorine, light green; cobalt, yellow; nitrogen, blue; oxygen, red.

TABLE IV. Synoptic collection of the unit cell parameters of complexes of the type *cis*-[M(phendione)$_2$X$_2$].

M	X	SPGR	a (Å)	b (Å)	c (Å)	V (Å^3)	T (K)	CCDC code	Reference
Cu	Br	$Fdd2$	41.330 (5)	8.3836 (19)	12.939 (3)	4482 (3)	298	GELWUQ	Stephenson and Hardie (2006)
Co	Cl	$Fdd2$	41.4951 (13)	8.2768 (2)	12.4494 (3)	4292.9 (2)	298	–	This work
Hg	Cl	$Fdd2$	42.6761 (11)[a]	8.2261 (2)[a]	12.6108 (3)	4427.1 (13)	120	DUKLOL	Figueiras *et al.* (2009)
Hg	Cl	$Fdd2$	42.098 (8)	8.3101 (8)	12.9061 (8)	4515.0 (16)	298	DUKLOL01	Ma *et al.* (2010)
Pb	I	$Fdd2$	54.701 (11)	8.2706 (17)	10.635 (2)	4811 (3)	293	ZOMVEE	Wu and Chen (2014)

[a]The unit cell parameters a and b were exchanged with respect to the original publication for the sake of comparison.

and *cis*-[Cu(phendione)$_2$Br$_2$] (Stephenson and Hardie, 2006) are known in the literature. *cis*-[Pb(phendione)$_2$I$_2$] (Wu and Chen, 2014) crystallizes in space group *Fdd*2; yet, despite the similar packing, it shows longer and smaller *a*- and *c*-axes, respectively, than those of the other three complexes (Table IV). These differences can be related to the longer I···π interaction [4.0998 (7) Å], which contributes to the lengthening of the *c*-axis. This lengthening increases the distance between the aromatic rings of adjacent complexes along *c*, and consequently favours a more effective herring-bone packing along *a*, reducing its length. In comparison, along *b* no closer packing is possible, which is supported by the small difference in length for the *b*-axis in the four cases.

IV. CONCLUSION

In this contribution, we have reported on the assessment of the crystal and molecular structure of the mononuclear complex *cis*-[Co$^{\mathrm{II}}$($\kappa^2 N,N'$-1,10-phenanthroline-5,6-dione)$_2$Cl$_2$] by PXRD with laboratory equipment.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715618000143

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