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Complexes of cobalt(II), nickel(II) and copper(II) with *ortho-* and *para-phenylenediamine* derivatives

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Abstract—Cobalt(II), nickel(II) and copper(II) complexes with BOP-H₂ (dibenzoinlidene-*o*-phenylenediamine) and BPP-H₂ (dibenzoinlidene-*p*-phenylenediamine) of general formulae $[M(H_2L)X_2]$, $[M_2(H_2L)_2X_4]$, [M(L)] and $[M_2(L)_2]$ (where M = Co, Ni, Cu; X = Cl or NO₃; H₂L and L are the neutral and dibasic forms of the ligands) have been prepared by the reaction of the corresponding metal salts with the two ligands in neutral and basic media. The complexes were characterised by elemental analysis, electrical conductance, magnetic susceptibility and spectral measurements. The studies revealed two different actions of the ligands, neutral tetradentate in neutral medium giving hexacoordinated metal atoms with octahedral geometry and dibasic tetradentate in alkaline solution giving tetrahedral and square planar structures © 1998 Elsevier Science Ltd. All rights reserved

Keywords: cobalt(II); nickel(II); copper(II); phenylene diamine derivatives.

A great deal of work has been reported on the synthesis and structural investigation of different types of Schiff bases and their complexes with transition and non-transition elements [1–6]. The importance of Schiff bases in their action as ligands is due to the ease and flexibility of their synthetic procedures as well as the sensitivity towards the central metal atom [7–9]. The majority of Schiff bases that give stable complexes usually act as multidentate N—N and N—O donors with the formation of mononuclear complexes. In some cases stable oxygen-bridges polynuclear complexes have been reported [6,10,11]. Aside from the interesting ligational properties, these Schiff bases have important biological activity [12–14].

We have reported previously the synthesis of many Schiff bases derived from the reactions of benzoin with acid hydrazides [5,6] or aminophenol [15]. In these complexes the ligands act as tri- and tetradentates forming mononuclear and oxygen-bridged binuclear complexes. In this paper we report the synthesis of Schiff bases derived from the reaction of benzoin with o- and p-phenylenediamine and the study of their complexes with cobalt(II), nickel(II) and copper(II).

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EXPERIMENTAL

Analysis and physical measurements

The complexes and the ligands were analysed for carbon, hydrogen and nitrogen using a 1106 CE microanalyser. Conductivity measurements were carried out using a 10^{-3} M solution in dimethylformamide on a LF-42 digital conductivity meter at 25°C. The magnetic susceptibility measurements were made by the Faraday method at room temperature using a Bruker BM6 instrument.

Diamagnetic corrections for the ligands were calculated using Pascal's constants [16]. Infrared absorption spectra were recorded on Pye-Unicam Sp-2000 and Sp-1100 spectrophotometers ($200-4000 \text{ cm}^{-1}$) as KBr discs. The electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution of the compounds in DMF at 25° C, using a 1 cm quartz cell.

MATERIALS AND METHODS

All the chemicals were of AnalaR. B.D.H., Aldrich or Fluka grade used without further purification. Synthesis of the ligands : the Schiff base ligands, BOP- H_2 and BPP- H_2 , were prepared by the reaction of *o*or *p*-phenylenediamine with benzoin (in 1:2 molar ratio) in absolute ethanol following the standard procedure reported for similar compounds [6].

Preparation of the complexes

The complexes were prepared by the following general procedure using the appropriate stoichiometries for the metal salt and ligand. A warm ethanolic solution of the metal salt (0.01 mol in 15 cm³) was added to a warm stirred ethanolic solution of the ligand (0.01 mol in 20 cm³). The resulting mixture was then treated in two different ways. In the first, the mixture was refluxed on a water bath for about 5-6 h. The solution was then evaporated to about half its volume and on cooling a crystalline product separated out. In the second method, 0.1 M potassium hydroxide was added slowly, with constant stirring, to the mixture till pH 8-8.5. At this pH complete precipitation occurred and the mixture was digested on a water bath for about 10 min and then cooled. The separated complexes from both methods were filtered off, washed with cold ethanol, diethylether and dried in vacuo.

RESULTS AND DISCUSSION

The new complexes were synthesized in good yield by the reaction of the metal salts with the two ligands in neutral and basic media according to the following equations:

$$MX_2 + BOP-H_2 \rightarrow [M(BOP-H_2)X_2]$$

$$2MX_2 + 2BPP-H_2 \rightarrow [M_2(BPP-H_2)_2X_4] \quad (1)$$

 $MX_2 + BOP-H_2 + 2KOH \rightarrow$

$$[M(BOP)] + 2KCl + 2H_2O$$

 $2\mathbf{M}\mathbf{X}_2 + 2\mathbf{B}\mathbf{P}\mathbf{P}\mathbf{H}_2 + 4\mathbf{K}\mathbf{O}\mathbf{H} \rightarrow$

$$[M_2(BPP)_2] + 4KX + 4H_2O$$
 (2)

where M = Co, Ni, Cu; X = Cl or NO₃; BOP-H₂ BPP-H₂ are the neutral forms of the ligands derived from o- and p-phenylenediamine, respectively, and BOP, BPP are the dibasic form of the same ligands. The complexes gave satisfactory analytical data (Table 1) indicating 1:1 metal-to-ligand stoichiometry for all of them. The complexes are air stable at room temperature but they decompose without melting at temperatures above 250°C. All the complexes are insoluble in water but they are soluble to a limited extent in methanol, ethanol, DMF and DMSO. Their low electrical conductances in DMF are consistent with the given formulation (Table 1) indicating non-electrolytic nature [17]. The active sites of the ligands and their coordination to the metal atoms as well as the structure of the resulting complexes were inferred by spectral and magnetic measurements.

Infrared spectra

The bonding of the ligands to the metal atom was characterised by comparison of the main infrared absorption bands of the free ligands and their complexes. Each ligand contains two symmetrical benzoinlidene groups (HO--C--C==N--) which show OH and C==N function in the same infrared region. The important bands of the free ligands and their complexes are given in Table 2.

For complexes formed in neutral medium (1), $[M(BOP-H_2)X_2]$ and $[M_2(BPP-H_2)_2X_4]$, the bands due to $\nu(OH)$ and $\delta(OH)$ vibrations showed negative shift of about 100–130 and 30–40 cm⁻¹, respectively, suggesting the involvement of alcoholic hydroxyle in coordination through their oxygen atoms.

The observation of a v(C-O) band at lower frequency by 30-40 cm⁻¹ and its splitting into two peaks M



(due to C—O—H) was considered to be further support for the coordinate of alcohol groups without deprotonation (Fig. 1) as observed in similar complexes [6]. The shifting of v(C—N) band to lower values by 25–30 cm⁻¹ indicates the participation of the two azomethine nitrogen atoms in bonding [8,9,18]. Additional bands, not observed in the free ligands' spectra located at about 1530, 1280 and 930 cm⁻¹ are attributed to vN—O of unidentate coordination of nitrato groups [19]. The chloro complexes exhibit bands in the range 280–290 cm⁻¹ and are assigned to the stretching frequency of coordinated chloride ions [20].

For 2 complexes formed in basic solution, [(BOP)] and $[M_2(BPP)_2]$, the disappearance of OH-stretching and deformation bands indicates the action of the ligands in their dibasic forms. This coordination was confirmed by the negative shift of the single v(C-O)band by 30–35 cm⁻¹. Furthermore, the C==N stretching bands in their complexes were lowered by 25– 30 cm⁻¹ and thus suggesting bond formation through azomethine groups similar to that observed in 1 complexes [8].

In both types, new bands were noticed in the infrared spectra at 440–450 and 480–485 cm⁻¹ and assigned to stretching modes of M—N and M—O, respectively [21,22].

Electronic spectra and magnetic moments

The μ_{eff} values and the positions of the electronic spectral bands together with the proposed geometries are given in Table 3. The electronic spectra of the complexes in DMF indicate two different structural configurations. For cobalt(II) complexes of 1, two bands were observed and assigned to ${}^{4}T_{1g}(F) \rightarrow$ ${}^{4}T_{2g}(F)(v_{1})$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)(v_{3})$ transitions, respectively, in an octahedral environment [23]. The

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No.	Complex	Colour	% Yield	$(cm^2 ohm^{-1} mol^-)$	С	Н	Ν
1	BOP-H ₂	Yellow-brown	96		82.6(82.3)	5.4(5.6)	5.3(5.6)
2	BPP-H ₂	Deep yellow	94		82.5(82.3)	5.8(5.6)	5.3(5.6)
3	$[Co(BOP-H_2)Cl_2]$	Brown	78	14	65.6(65.2)	4.3(4.5)	4.4(5.5)
4	$[Ni(BOP-H_2)NO_2)_2]$	Brown	76	6	60.3(60.1)	4.3(4.1)	8.4(8.2)
5	[Cu(BOP-H ₂)Cl ₂]	Deep yellow	80	10	65.1(64.7)	4.6(4.4)	4.4(4.4)
6	$[Co_2(BPP-H_2)_2Cl_4]$	Pale brown	68	12	65.5(65.2)	4.4(4.5)	4.6(4.5)
7	$[Ni_2(BPP-H_2)(NO_3)_4]$	Brown	74	7	60.5(60.1)	4.0(4.1)	8.3(8.2)
8	$[Cu_2(BPP-H_2)_2Cl_4]$	Pale brown	70	4	64.2(64.7)	4.1(4.4)	4.2(4.4)
9	$[Co(BOP)]^a$	Deep yellow	86	3	74.1(73.8)	4.6(4.7)	4.8(5.1)
10	[Ni(BOP)] ^a	Light brown	84	8	73.5(73.8)	4.5(4.7)	4.7(5.1)
11	[Cu(BOP)]"	Light brown	84	5	72.9(73.2)	4.8(4.7)	5.2(5.0)
12	$[Co_2(BPP)_2]^a$	Brown	80	10	73.4(73.8)	4.3(4.7)	5.3(5.1)
13	$[Ni_2(BPP)_2]^{\alpha}$	Deep yellow	87	6	74.2(73.8)	4.6(4.7)	5.2(5.1)
14	$[Cu_2(BPP)_2]^{\prime\prime}$	Pale brown	81	5	73.5(73.2)	4.9(4.7)	5.4(5.0)

Table 1. Analytical data and some physical properties

"The same compound was obtained by using different metal salts.

Compound No.	v (OH)	v (C==N)	δ (OH)	v (C—O)	v (M—N)	v (M—O)	$(\mathbf{M}-\mathbf{X})^{h}$
1	3500	1635	1310	1240			
2	3500	1635	1320	1240			
3	3380	1610	1280	1200 1205	440	485	285
4	3385	1605	1275	1200 1205	440	485	1530, 1280, 930
5	3400	1605	1280	1200 1210	445	485	285
6	3385	1610	1280	1205 1210	450	480	290
7	3390	1605	1285	1200 1210	450	485	1525, 1280, 935
8	3390	1605	1280	1200 1205	445	485	280
9		1610		1210	440	480	
10	_	1610		1210	440	480	
11		1605		1210	440	485	_
12		1610		1205	440	485	_
13		1610		1205	450	485	
14		1605		1210	450	485	

Table 2. Important IR spectral data (cm⁻¹)

"As in Table 1.

 b X = Cl or NO₃.

 v_2 band due to ${}^4T_1g(F) \rightarrow {}^4A_2g(F)$ transition could not be observed, as it is a two electron process and is much weaker than the other two transitions [24]. Therefore the v_2 transition remain almost unobserved because of its weakness and proximity to a strong v_3 transition [25]. However the values of v_2 bands have been calculated and the results are in good agreement with Tanabe–Sugano diagram for a d^7 ion in an octahedral environment where v_2 and v_3 transitions are predicted to lie almost at the same position [26]. The electronic spectra of nickel(II) complexes of 1 exhibit three bands attributed to v_1 , v_2 and v_3 which correspond to the transitions ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)$, ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)$ and ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)$, respectively. The spectra of both nickel(II) complexes referred to considerable distortion for octahedral symmetry (not observed for



cobalt(II) complexes) since the calculated energy difference between ${}^{3}T_{1}g(P)$ and ${}^{3}T_{1}g(F)$ levels (14,500 cm⁻¹) is greater by about 5200 cm⁻¹ than the difference $v_{3}-v_{2}$ (~9300 cm⁻¹). This is presumably due to interligand interaction and repulsion causing elongation of metal–ligand bonds and thus leading to distortion of the octahedron [27]. In the case of copper(II) 1 complexes a broad asymmetric band was observed and assigned to the three combined transitions ${}^{2}B_{1}g \rightarrow {}^{2}A_{1}g$, ${}^{2}B_{1}g \rightarrow {}^{1}B_{2}g$ and ${}^{2}B_{1}g \rightarrow {}^{2}Eg$ of tetragonally distorted octahedral environment around copper(II) ion due to the Jahn–Teller effect [28–30].

The effective magnetic moments for BOP-H₂ complexes measured at room temperature fall in the range expected for high-spin octahedral geometries [31] for cobalt(II), d^7 , nickel(II), d^8 , and copper(II), d^9 , systems consistent with the presence of three, two and one unpaired electrons, respectively. On the other hand, the μ_{eff} values for BPP-H₂ complexes were less than those expected. The lower values may be attributed to binuclear dimeric structure as observed for similar complexes and ascribed as antiferromagnetic coupling of the unpaired electrons on the adjacent metal ions [32].

The complexes of 2 exhibit two different geometries as found from the electronic spectra and magnetic moments. Cobalt(II) and nickel(II) complexes exhibit two bands due to ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(P)$. ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$ and ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(F)$, ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ transitions and assigned to v_2 and v_3 , respectively. The low energy transition ${}^{4}T_{2}(F) \rightarrow {}^{4}T_{2}(F)$ and ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{2}(F)$ of the unobserved band v_1 was theoretically calculated [24]. The positions and intensity of these bands are consistent with tetrahedral geometry for the tetracoordinated cobalt(II) and nickel(II) complexes [23]. For copper(II) complexes, only one broad band was observed in their electronic spectra. This band is attributed to the ${}^{2}B_{1}g \rightarrow {}^{2}Eg$ transition which is consistent with square planar geometry around the copper(II) ion [33]. Once again, all the complexes were found to be paramagnetic with magnetic moments (Table 3), for BOP-complexes consistent with three, two and one unpaired electron, while for BPP-complexes lower μ_{eff} values were observed (as in 1) and attributed to superexchange mechanism.

From the above discussion and on the bases of the data given in Tables 1–3, the following conclusion can be drawn. Both ligands act as tetradentate forming hexacoordinate complexes (in neutral medium) with most probable octahedral or distorted octahedral

Compound	Electronic bands (cm ⁻¹)			Magnetic moments	
No."	v ₁	<i>v</i> ₂	<i>v</i> ₃	(BM)	Geometry
3	9240	18,800*	19,600	4.0	Octahedral
4	8900	15,850	25,150	3.11	Distorted octahedral
5	13,800	_		1.95	Distorted octahedral
6	9260	18,820	19,650	3.58	Octahedral
7	8950	15,988	25220	1.66	Distorted octahedral
8	14,100			1.58	Distorted octahedral
9	3250"	6500	14,500	3.95	Tetrahedral
10	3950"	7100	13,950	3.10	Tetrahedral
11	24,100			1.95	Square planar
12	3280'	6550	14,550	3.65	Tetrahedral
13	4000*	7150	14,000	2.60	Tetrahedral
14	24,300			1.65	Square planar

Table 3. Magnetic moments, electronic spectral data and proposed geometries

"As in Table 1.

^bCalculated values.



structures. In basic medium, they act as dibasic tetradentate forming tetrahedral and probably distorted planar [for cobalt(II) and nickel(II)] and square planar [for copper(II)] complexes. Mononuclear complexes were obtained with BOP ligand, while BPP acts as bridging ligand forming dinuclear complexes as shown in Figs 1 and 2.

REFERENCES

- 1. Yamada, S., Coord. Chem. Rev., 1966, 1, 415; 1967, 2, 83.
- Kahwa, I. A., Hsieh, T. C. Y., Laine, R. A. and Selbin, J., *Inorg. Chim. Acta*, 1986, 118, 179.
- Golonka, M. C. and Bartecki, A., Coord. Chem. Rev., 1979, 31, 251.
- O'Conner, C. J., Romananch, R. J., Robertson, D. M. Edudk, E. E. and Fronczek, F. F., *Inorg. Chem.*, 1983, **22**, 449.
- 5. Sallomi, I. J. and Shaheen, A. J., *Iraqi J. Chem.*, 1990, **15**, 129.

- 6. Sallomi, I. J. and Shaheen, A. J., *Trans. Met. Chem.*, 1994, **19**, 275 and refs therein.
- Bomlneri, G., Benetoilo, F., Pollo, A., De Cola, L., Smales, D. L. and Vallarino, I. M., *Inorg. Chem.*, 1986, **25**, 1127.
- Dey, K., Ray, S., Bhattacharyya, P. K., Gangopadhyay, A., Bhasin, K. K. and Verma, R. D., *J. Indian Chem. Soc.*, 1985, **62**, 809.
- Sallomi, I. J. and Shaheen, A. J., J. Iraqi Chem. Soc., 1987, 12, 159.
- Padhye, S. and Kauffman, G. B., Coord. Chem. Rev., 1985, 63, 127.
- 11. Sinn, E. and Harris, C. M., Coord. Chem. Rev., 1969, 4, 391.
- Hodnett, E. M. and Dunn, W. J., J. Med. Chem., 1970, 12, 768.
- Hodnett, E. M. and Moony, P. D., J. Med. Chem., 1970, 13, 786.
- Billman, H. J. and Schrmidgall, R. L., J. Pharm. Sci., 1970, 59, 1191.
- 15. Sallomi, I. J., Trans. Met. Chem., in press.
- Selwood, P. W., Magnetochemistry. Interscience, New York, 1956.
- 17. Geary, W. J., Coord. Chem. Rev., 1971, 7, 81.
- Taylor, L. T. and Patton, R. D., Inorg. Chim. Acta., 1974, 8, 191.
- Gatehouse, B. M., Livingston, S. E. and Nyholm, R. S., J. Chem. Soc., 1957, p. 4222; J. Inorg. Nucl. Chem., 1958, 8, 75.
- 20. Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds. New York, 1983.
- 21. Madan, S. K. and Donohus, A. M., J. Inorg. Nucl. Chem., 1969, 28, 1303.
- 22. Fay, R. C. and Pinnavaia, T. J., Inorg. Chem., 1968, 7, 502.
- 23. Lever, A. B. P., Inorganic Electronic Spectroscopy. Elsevier, Amsterdam, 1968.
- 24. Lever, A. B. P., J. Chem. Ed., 1968, 45, 711.
- 25. Ram Rao, N., Surya Rao, D. and Ganorkar, M. C., *Indian J. Chem. Sect. A.*, 1982, **21**, 839.
- 26. Lever, A. B. P., J. Chem. Soc., A, 1967, p. 241.
- 27. Sallomi, I. J., J. Indian Chem. Soc., 1995, 72, 327.
- Jahn, H. A. and Teller, E., Proc. Roy. Soc. (London), 1937, 161, 220.
- 29. Duff, E. J., Hughes, M. N., and Rutt, K. J., J. Chem. Soc., 1969, p. 2126.
- Satyanarayana, D. and Mahapatra, B. K., Indian J. Chem., 1975, 13, 414.
- 31. Figgis, B. N. and Lewis, J., Prog. Inorg. Chem., 1964, 6, 37.
- McLellan, A. W. and Melson, G. A., J. Chem. Soc., A, 1967, p. 137.
- 33. Ferguson, J., Theor. Chim. Acta., 1965, 3, 287.