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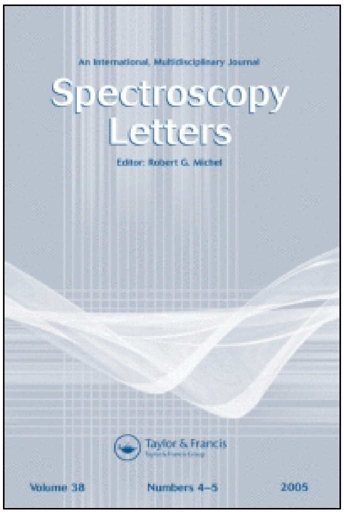

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SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH SCHIFF BASES DERIVED FROM 2-HYDROXYACETYLACETOPHENONE

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SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH SCHIFF BASES DERIVED FROM 2-HYDROXYACETYLACETOPHENONE

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ABSTRACT

Metal chelates of some Schiff bases derived from diamines and 2-hydroxyacetylacetophenone with Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+} of stoichiometric ratios 1:1 and 2:1 (M:L) have been synthesized and characterized by different spectrophotometric techniques. It is found that the coordination site of ligands differs depending on the kind of metal ions. Thus, Cr^{3+}, Fe^{3+}, and Co^{2+} enter in the outer O_2O_2 compartment, whereas Ni^{2+}, Cu^{2+}, and Cd^{2+} enter into N_2O_2 site. The g-values of Cu^{2+} complexes suggest square-planar geometry; this is confirmed from the ESR spectra of its complexes.

Key Words: Elemental analysis; Spectra; Transition metals; 2-Hydroxyacetylacetophenone Schiff bases

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INTRODUCTION

The study of transition metal complexes with Schiff bases drew the attention of many workers (1) due to their analytical and biological applications. The synthesis, characterization, and antimicrobial activities of some dipositive 3d-metal ion chelates of furfurylidenenicotinamide Schiff base was reported (2). Co^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} complexes of Schiff bases with N and S donor sites have been prepared and studied (3). Metal complexes of 4-amino-3,5-dimercapto-1,2,4-triazole have been investigated (4). The aim of the present study is to prepare and characterize the complexes of some Schiff bases derived from ethylenediamine, 1,3-propylenediamine, *o*-phenylenediamine, and 2-hydroxyacetylacetophenone with Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}.

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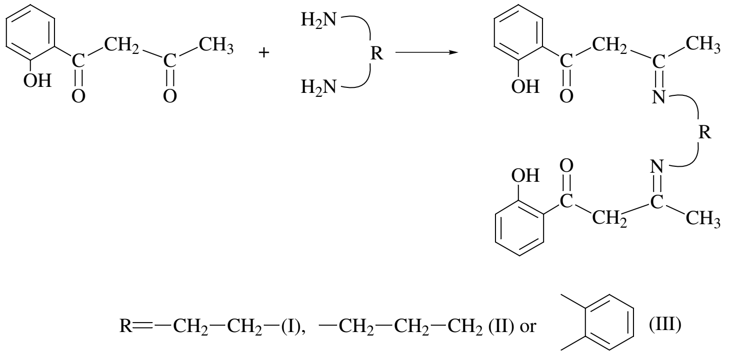
EXPERIMENTAL

All chemicals used were of high purity grade (from BDH or Fluka) and were used without further purifcation. The Schiff bases were prepared by condensation of 2-hydroxyacetylacetophenone (0.02 *M* in 50 mL ethanol) with the diamines, ethylenediamine, 1,3-propylenediamine, and *o*-phenylenediamine (0.01 *M* in 50 mL ethanol), as previously recommended (5). The reaction takes place as follows:



R = $-CH_2-CH_2-$ (I), $-CH_2-CH_2-CH_2$ (II) or (III)

The crude products, separated on cooling, were crystallized from CCl_4 for compound I, or from benzene for compounds II and III. The purity was then checked by melting point constancy, elemental analysis (as C, H, and N), infrared spectroscopy, and ^1H NMR spectroscopy.

The solid complexes were prepared by mixing hot ethanolic solutions of Schiff bases (0.01 *M* in 60 mL) and 0.01 or 0.02 *M* of metal chloride (in 20 mL H_2O and 20 mL ethanol). Each mixture was refluxed for about 6 h on water bath then allowed to cool whereby the solid chelates were separated, crystallized from absolute ethanol, and dried in a desiccator over P_2O_5.

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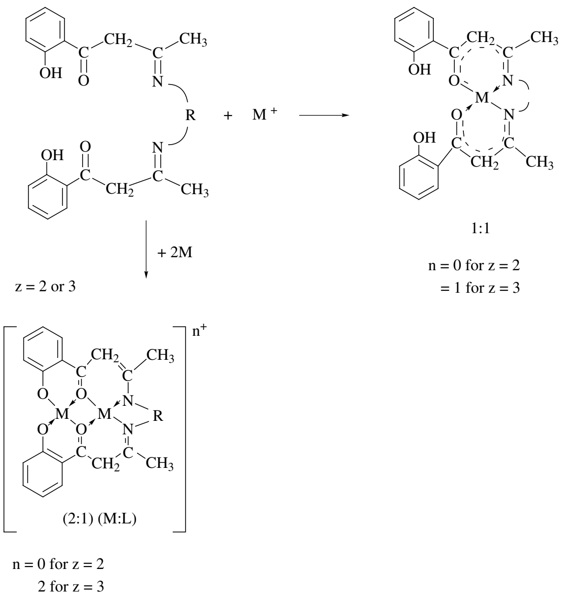
Elemental analysis (C, H, and N) for metal complexes were carried out in microanalysis center, Cairo University, Giza, Egypt. The metal ion contents (M%) were performed by EDTA titration under the appropriate conditions (6).

The molar conductance (Λ_M) was measured by dissolving the solid chelates in DMF to a certain molar concentration, using YSI model 32 conductance meter of cell constant $K = 1$. The IR spectra of the free ligands and their metal complexes were measured using a Beckman IR 4200 double beam spectrophotometer within the range 4000–200 cm^{-1}, using KBr disc. The ^1H NMR spectra of the free ligands and their Cd^{2+} complexes were recorded on a Varian PMx 60 SI NMR spectrometer, using TMS as internal standard and DMSO-d_6 as a solvent. Electronic absorption spectra (UV–vis) were measured by Perkin-Elmer Lambda 3B spectrophotometer, using DMF as solvent for metal complexes, and also nujol-mull technique was used. The ESR spectra of some selected Cu^{2+} complexes were measured using a Varian EGI-x-band spectrometer equipped with an E 101 microwave bridge.

RESULTS AND DISCUSSION

The complexation reaction taking place between the metal ions and ligands under consideration is expected to occur according to Scheme 1:



Scheme 1.

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Table 1. Elemental Analysis Data of the Schiff Base Derivatives Under Investigation

Ligand	Molecular Weight	Solvent of Crystallization	Color	Melting Point (°C)	C% Found	C% Calc.	H% Found	H% Calc.	N% Found	N% Calc.
I	380.44	Carbon tetrachloride	Yellow	190–192	70.11	69.46	6.52	6.36	7.15	7.36
II	428.49	Benzene	Yellow	107–109	72.20	72.88	5.75	5.65	6.33	6.54
III	394.47	Benzene	Yellow	125–127	70.30	69.96	6.46	6.64	7.00	7.10

Calc. = Calculated.

A majority of complexes are insoluble in common organic solvents but soluble in DMF. Elemental analysis (C, H, N, and M) are in good agreement with the expected formula (Tabs. 1 and 2). The presence of anion (Cl^-) inside or outside the coordination sphere was confirmed by the precipitation of AgCl on the addition of $AgNO_3$ to the solubilized chelates in DMF. The molar conductance measurements show that all 1:1 and 2:1 (M:L) complexes of divalent metal ions are nonelectrolytic, whereas an electrolytic nature is observed for Cr^{3+} and Fe^{3+} complexes. The nonelectrolytic nature of divalent complexes is supported by their insolubility in common organic solvents.

The spectral data obtained from UV–vis measurements for the most complexes in nujol mull and DMF show a λ_{max} not more than 270 nm (~37,000 cm^{-1}).

The IR spectra of Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+} dehydrated complexes are studied and compared to those of free ligands. Inspection of the IR spectra shows that

a. The spectra of 1:1 complexes of Ni^{2+}, Cu^{2+}, and Cd^{2+} show a broad band within the range 3427–3399 cm^{-1}, which is due to the stretching vibration of OH group (ν_{OH}). This band is not observed in the case of Cr^{3+}, Fe^{3+}, and Co^{2+} dehydrated complexes. Thus, it seems that the latter ions coordinate to ligand molecules through the hydroxyl groups of the arylidene moieties. This is supported by the appearance of the ν_{M-O} bands in the range 363–327 cm^{-1}. On the other hand, dehydrated complexes of Ni^{2+}, Cu^{2+}, and Cd^{2+} show a band within the range 482–433 cm^{-1} due to ν_{M-N} stretching vibration (Tab. 3).

b. The spectra of Schiff bases show an intense band due to the $\nu_{C{=}O}$ group at 1719, 1720, and 1615 cm^{-1} for ligands I, II, and III, respectively. This band is markedly shifted to the lower frequency side on complex formation, which is taken as an evidence for the participation of the C=O groups in the complexation process as shown in Table 3.

c. The stretching vibration frequencies of the C=N group of the free ligands are found at 1655, 1650, and 1598 cm^{-1} for ligands I, II, and III, respectively. This band is shifted to lower frequencies in the case of Ni^{2+}, Cu^{2+}, and Cd^{2+}.

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Table 2. Chemical Analysis of Metal Chelates of Ligands (I–III) Under Investigation

Compound	Ratio M:L	Color	M% Found	M% Calc.	H_2O% Found	H_2O% Calc.	Δm (Ω^{-1}) (Calc.)	Chemical Formula
Cu^{2+}–I	1:1	Blue	13.40	13.29	7.50	7.53	15.60	$Cu–L_{I}–2H_2O$
	2:1	Blue	22.20	22.08	12.50	12.51	12.50	$Cu_2–L_{I}–4H_2O$
Cu^{2+}–II	1:1	Dark blue	12.10	12.08	6.95	6.85	13.60	$Cu–L_{II}–2H_2O$
	2:1	Brown	20.40	20.38	11.50	11.55	13.06	$Cu_2–L_{II}–4H_2O$
Cu^{2+}–III	1:1	Blue	12.76	12.92	7.39	7.32	12.26	$Cu–L_{III}–2H_2O$
	2:1	Blue	12.81	21.56	12.36	12.22	11.24	$Cu_2–L_{III}–4H_2O$
Co^{2+}–I	1:1	Dark green	12.61	12.45	7.69	7.61	11.24	$Co_2–L_{III}–4H_2O$
	2:1	Dark green	20.91	20.81	12.88	12.72	10.94	$Co_2–L_{I}–4H_2O$
Co^{2+}–II	1:1	Brown	11.23	11.30	7.15	6.91	11.80	$Co_2–L_{II}–2H_2O$
	2:1	Black	19.38	19.18	11.91	11.72	11.66	$Co_2–L_{II}–4H_2O$
Co^{2+}–III	1:1	Green	12.16	12.09	7.06	7.39	10.60	$Co_2–L_{III}–2H_2O$
	2:1	Green	20.50	20.31	12.19	12.41	10.60	$Co_2–L_{III}–4H_2O$
Ni^{2+}–I	1:1	Buff	12.66	12.41	7.95	7.61	10.67	$Ni_2–L_{I}–2H_2O$
	2:1	Buff	20.89	20.31	12.93	12.73	10.48	$Ni_2–L_{I}–4H_2O$
Ni^{2+}–II	1:1	Black	11.20	11.26	6.75	6.91	11.16	$Ni_2–L_{II}–2H_2O$
	2:1	Black	19.01	19.12	11.36	11.73	10.26	$Ni_2–L_{II}4H_2O$
Ni^{2+}–III	1:1	Brown	12.22	12.05	7.51	7.39	10.56	$Ni_2–L_{III}–2H_2O$
	2:1	Green	20.36	20.24	12.61	12.42	10.35	$Ni_2–L_{III}–4H_2O$
Cd^{2+}–I	1:1	Yellow	21.20	21.34	6.90	6.84	10.31	$Cd–L_{I}–2H_2O$
	2:1	Yellow	33.29	33.29	10.73	10.60	9.92	$Cd_2–L_{I}–4H_2O$
Cd^{2+}–II	1:1	White	19.50	19.55	6.30	6.26	10.42	$Cd–L_{II}–2H_2O$
	2:1	Pale white	31.15	31.17	9.80	9.99	10.24	$Cd_2–L_{II}–4H_2O$
Cd^{2+}–III	1:1	Yellow	20.70	20.78	6.70	6.66	10.17	$Cd–L_{III}–2H_2O$
	2:1	Yellow	32.60	32.17	10.50	10.48	9.89	$Cd_2–L_{III}–4H_2O$
Cr^{3+}–I	1:1	White	10.79	10.74	3.60	3.72	13.39	$Cr–L_{I}–H_2O–Cl$
	2:1	Pale green	11.75	17.73	6.02	6.14	13.03	$Cr_2–L_{I}–2H_2O_2–Cl$
Fe^{3+}–I	1:1	Buff	11.31	11.45	3.81	3.69	12.54	$Fe–L_{I}–H2O–Cl$
	1:2	Red	18.77	18.80	6.15	6.06	12.43	$Fe_2–L_{I}–2H_2O_2–Cl$

Calc. = Calculated.

On the other hand, the IR spectra of all 2:1 (M:L) dehydrated complexes show the shift of both $\nu_{C=N}$ and $\nu_{C=O}$ to lower frequency side as compared to those of the free ligands, together with the appearance of new bands within the ranges 315–375 and 429–474 cm^{-1} due to the ν_{M-O} and ν_{M-N} frequencies, respectively, leading to the confirmation that complexation process takes place in an $N_2O_2O_2$ fashion with a mode of chelation as

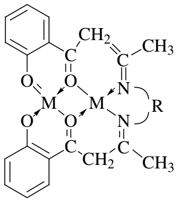

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Table 3. The IR-Vibrational Bands of Functional Groups of Ligands (I–III) and Their Metal Chelates

Compound	Ratio	ν_{OH}	δ_{OH}	$\nu_{C=O}$	ν_{N-H}	ν_{M-O}	ν_{M-N}
I	–	3427	1296	1719	3528	–	–
Cu^{2+}–I	1:1	3445	1314	1567	–	372	475
	2:1	3456	1310	1567	–	375	474
Co^{2+}–I	1:1	3430	1329	1620	3505	342	–
	1:2	3438	1329	1600	–	337	459
Ni^{2+}–I	1:1	3448	1346	1670	–	357	457
	2:1	3472	1346	1637	–	350	458
Cd^{2+}–I	1:1	3434	1342	1606	–	370	436
	1:2	3433	1339	1605	–	363	435
Cr^{3+}–I	1:1	3451	1347	1678	3500	351	–
	2:1	3461	1318	1670	–	342	459
Fe^{3+}–I	1:1	3439	1333	1685	3496	362	–
	2:1	3446	1326	1680	–	356	439
II	–	3399	1343	1615	3440	–	–
Cu^{2+}–II	1:1	3445	1359	16.08	–	346	436
	2:1	3444	1368	1615	–	316	433
Co^{2+}–II	1:1	3415	1360	1619	3381	331	–
	2:1	3413	1361	1609	–	327	436
Ni^{2+}–II	1:1	3448	1352	1620	–	311	439
	2:1	3451	1351	1618	–	315	439
Cd^{2+}–II	1:1	3402	1359	1612	–	337	434
	2:1	3409	1358	1610	–	342	429
III	–	3424	1316	1720	3488	–	–
Cu^{2+}–III	1:1	3435	1315	1580	–	342	411
	2:1	3451	1309	1598	–	341	419
Co^{2+}–III	1:1	3432	1335	1609	3482	365	–
	2:1	3431	1335	1610	–	367	439
Ni^{2+}–III	1:1	3434	1342	1645	–	353	482
	2:1	3433	1337	1621	–	380	457
Cd^{2+}–III	1:1	3434	1339	1609	–	344	422
	2:1	3441	1338	1611	–	360	424
Cr^{3+}–III	1:1	3451	1334	1597	3480	356	–
	2:1	3435	1337	1591	–	362	446

The ^{1}H-NMR spectra of the free ligands are studied and compared to those of their Cd^{2+} complexes. For the free ligands the multiple signals appearing at $\delta = 2.33$–2.9 ppm are due to the three protons of the CH_3 groups, whereas the broad multiple signals at $\delta = 6.2$–7.65 ppm are due to the four aromatic protons of each ring. The singlet signal at $\delta = 10.52$–11.2 ppm (removed by deuteration)

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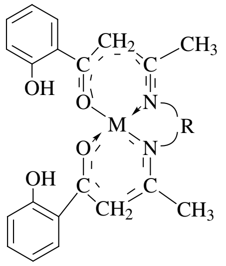
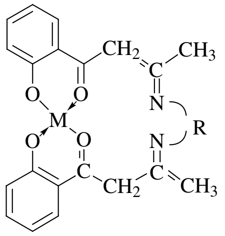
is due to the proton of the hydroxyl group. This signal did not disappear in the case of Cd^{2+} complexes, but slightly shifted upfield due to chelate formation. This supports the N_2O_2 fashion for Cd^{2+} complexes, complexes that are formed due to the delocalization of π electrons as a result of coordinate bond between metal ions and nitrogen atom. Thus, it is clear that the coordination sites of these ligands differ depending on the kind of metal ions, where it is found that Cr^{3+}, Fe^{3+}, and Co^{2+} interact through the O_2O_2 site but Ni^{2+}, Cu^{2+}, and Cd^{2+} interact in an N_2O_2 fashion. This can be explained in terms of a soft and hard acid and base concept (7–12). It is known that Cr^{3+}, Fe^{3+}, and Co^{2+} ions are harder than Ni^{2+}, Cu^{2+}, and Cd^{2+} ions, and the oxygen atom is harder than the nitrogen atom. So, the former ions prefer an O_2O_2 site type for coordination, whereas the later ions prefer an O_2N_2 site (13–18). Thus, the mode of chelation of 1:1 complexes can be represented as



M = Ni(II), Cu(II) and Cd(II)



M = Cr(III), Fe(III) or Co(II)

The ESR spectra of solid complexes at room temperature is a characteristic of a compound having an axial type symmetry with $d_{x^2-y^2}$ ground state, which is the most common for copper (II) complexes (19,20). The lack of hyperfine structure in the spectra suggests that intermolecular exchange interactions are operative. This is further supported by the g-value which is lower than 4 ($g = 2.8$) (21). The g-values suggest square-planar geometry around the copper ion with covalent bond character (22) in the case of ligand (I); the ESR parameters are $g_{11} = 2.\ 14$, $g_1 = 2.05$, $g_{\mathrm{iso}} = 2.08$, and $G = 2.8$. The ESR spectrum of copper (II) complex with ligand (II) in solid state at room temperature shows nonaxial symmetry with three g-values: $g_1 = 2.17$, $g_2 = 2.11$, and $g_3 = 2.08$. The g-values suggest square-planar structure with d_{x2-y2} ground state (23,24). The ESR spectrum of copper (II) complex with ligand (III) gives an isotropic signal in the low field region with $g_{\mathrm{iso}} = 2.09$ indicating square-planar geometry around copper (II) ion (22).

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REFERENCES

1. Sinha, B.K.; Kumar, M.; Kumar, R.; Bbtacharjee, N.C. J. Indian Chem. Soc. **1995**, *2*, 623.
2. Srivastava, V.; Srivastava, S.K.; Mishra, A.P. J. Indian Chem. Soc. **1995**, *72*, 47.
3. Bhaskare, C.K.; Hankare, P.P. J. Indian Chem. Soc. **1995**, *72*, 585.
4. Sinha, B.K.; Singh, R.; Srivastava, J.P.; Mishra, L.K. J. Inorg. Nucl. Chem. **1977**, *39*, 1797.
5. Bassett, J.; Danneg, R.C.; Jeffery, B.H.; Mendbam, J. Vogel Text Book of Quantitative Inorganic Analysis, (4th Ed.,) 1978; 302–304.
6. Wileher, F.J. The Analytical Uses of Ethylene Diaminebetraceric Acid D.Van Nostrand: Princeton, NJ, 1965.
7. Genery, W.J. Coord. Chem. Ref. **1971**, *7*, 81.
8. Lever, A.B.P.; Ramaswamy, B.S. Can. J. Chem. **1973**, *15*, 514.
9. Misbra, N.C. J. Indian Chem. Soc. **1978**, *55*, 839.
10. Nakamote, K. Obkaku Inorg. Chem. **1971**, *10*, 817.
11. Kanig, E. Inorg. Chem. **1971**, *10*, 2632.
12. Shallaby, A.M.; Mostafa, M.M.; Bekeit, M.M. Indian J. Chem. **1979**, *17*, 16.
13. Lever, A.B.P.; Montavani, B. Inorg. Chem. **1971**, *10*, 817.
14. Janse, D.W.; Molan, M.J. Prog. Inorg. Chem. **1968**, *9*, 195.
15. Nakamoto, K.I.; Bebwke, G.T. Inorg. Chem. **1967**, *6*, 433.
16. Persen, R.G.; J. Amer Chem. Soc. **1963**, *85*, 3533.
17. Yene, T.; Vshijima, T.; Veno, K. Bull. Chem. Soc. **1972**, *45*, 2452.
18. Tomlanovic, B.; Raymand, L.; Glick, H.M. J. Amer. Chem. Soc. **1971**, *97*, 14.
19. Eisenstein, J.C. J. Chem. Phys. **1959**, *58*, 323.
20. Hathaway, B.J.; Billing, T.E. Coord. Chem. Rev. **1970**, *5*, 143.
21. Procter, I.M.; Hathaway, B.J.; Nicholls, P.N. J. Chem. Soc. **1969**, 1678.
22. Ray, R.K. Inorg. Chim. Acta **1990**, *174*, 257.
23. Kivelson, D.; Neiman, R. J. Chem. Phy. **1961**, *35*, 149.
24. Shazly, M.; Dissowky, A.; Salem, T.; Osman, M. Inorg. Chim. Acta, **1980**, *40*, 1.

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