Indian Journal of Chemistry
Vol. 15A, April 1977, pp. 324-326

Studies on Mixed Ligand Complexes Containing β-Dicarbonyls: Part II—Complexes of Cu(II) & Ni(II)

UMA DORASWAMY & P. K. BHATTACHARYA
Chemistry Department, M.S. University of Baroda, Baroda 2

Received 15 *March* 1976; *accepted* 22 *August* 1976

Mixed ligand complexes of the type (MLL′) where M=Cu(II) or Ni(II), LH=salicylaldehyde and L′H=benzoylacetone or dibenzoylmethane have been prepared. On treatment of (MLL′) with ammonia, methyl- or ethyl amine, only the salicylaldehyde part of the molecule forms Schiff base, the β-diketone part remaining unreacted. This schiff base complex can also be prepared by treating the metal-amine complex with an equivalent amount of salicylaldehyde and β-diketone. Amine-exchange reactions have also been carried out. The salicylaldehyde part reacts with ethanolamine to form schiff base, while the β-diketone part is removed in the case of Cu(II) complex. The complexes have been characterized on the basis of elemental analyses, TLC, conductance, magnetic moment and spectral studies.

IN continuation of our earlier work[1] on mixed ligand complexes of the type (MLL′) where LH = salicylaldehyde and L′H = acetylacetone, we report in this paper mixed ligand complexes of the type (MLL′) where M = Ni(II) or Cu(II), LH = salicylaldehyde, L′H = benzoylacetone (BA) or dibenzoylmethane (DBM). The reactions of the complexes with ammonia, alkyl amines and ethanol amine have also been investigated.

Materials and Methods

The compounds (I) and (II) were prepared in the same way as reported earlier[1].

Reactions of mixed ligand complexes with ethanolamine — Cu(II) mixed ligand complexes containing salicylaldimine and β-diketone were treated with a slight excess of monoethanolamine. The mixed ligand compound dissolved and the solution was refluxed on a water-bath. The product was obtained by pouring water into the reflux. In the case of Ni(II), solid did not dissolve on addition of ethanolamine. The completion of the reaction was judged by change in colour of the solid on refluxing. In both the cases the solid was filtered, washed with water and finally with 50% ethanol. The Cu(II) complexes were recrystallized from absolute ethanol. The Ni(II) complexes have very low solubility and could not be recrystallized. The analytical data of the complexes are shown in Table 1. Conductance, TLC, magnetic measurements and spectral studies were carried out as reported earlier[1].

Results and Discussion

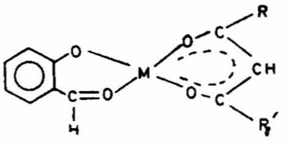
On treatment with excess ammonia or alkyl amines, mixed ligand complexes (I) give mixed Schiff base complexes (II).

The coordinated aldehyde in(I) undergoes reaction with primary amines to form Schiff bases. The coordinated aldehyde becomes more susceptible to nucleophilic attack[2] due to coordination with the metal ion. The diketones however remain unaffected because coordinated diketones have very little tendency to undergo Schiff base formation due to delocalization of π-electrons over the whole chelate ring which gives it a *pseudo*-aromatic character[3]. As a result of this the reactivity of the carbonyl group is very much reduced.

Compound II (R$''$ =H) could also be prepared by adding a mixture of the two ligands to the metal-amine complex solution, such that the metal and the two ligands were in equimolar ratio. Here the Schiff base formation involving condensation of salicylaldehyde with coordinated amine group is facilitated due to the template effect[4].

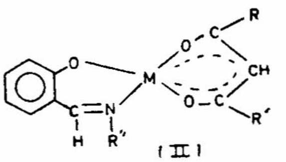
Compound II (R$''$ = CH_3 or C_2H_5) could be obtained by amine exchange with II (R$''$=H).

The amine-exchange reaction proceeds by a nucleophilic attack of the exchanging amine on the electron deficient carbon of the polarized imine. A more basic amine (which is more nucleophilic) replaces a less basic amine from the Schiff base. The reaction is, however, concentration dependant also. A higher concentration of less basic amine may replace the more basic amine from the Schiff



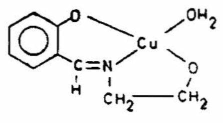
(I)

M = Cu(II)or Ni(II);
R=CH_3, R′=C_6H_5

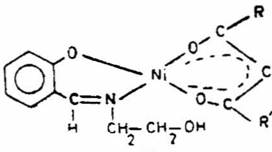


(II)

M=Cu (II)or Ni (II); R=CH_3 or C_6H_5
R′=C_6H_5 ; R″=H, CH_3 or C_6H_5



(III)



(IV)
R=CH_3or C_6H_5, R′=C_6H_5

TABLE 1 — ANALYTICAL AND PHYSICOCHEMICAL DATA OF Cu(II) AND Ni(II) MIXED LIGAND AND MIXED SCHIFF BASE COMPLEXES

Complex	Found (Calc.), %		λ_{max} (nm)	ϵ (mole/cm)	μ_{eff} (BM)
	M	N			
(Benzoylacetonato) (salicylaldehydato)Cu(II)	18·47 (18·39)	—	650	48	1·90
(Benzoylacetonato) (salicylaldimino)Cu(II)	18·59 (18·44)	4·12 (4·06)	630	70	1·94
(Benzoylacetonato) (salicylaldimino)Ni(II)	17·09 (17·28)	4·08 (4·12)	550	—	2·59
(Dibenzoylmethanato) (salicylaldimino)Cu(II)	15·49 (15·63)	3·56 (3·44)	640	80	1·87
(Dibenzoylmethanato) (salicylaldimino)Ni(II)	14·53 (14·61)	3·23 (3·48)	550	—	2·57
(Benzoylacetonato) (N-methylsalicylaldimino)Cu(II)	17·54 (17·71)	3·81 (3·90)	630	72	1·93
(Benzoylacetonato) (N-ethylsalicylaldimino)Cu(II)	16·33 (16·44)	3·54 (3·62)	640	65	1·87
(Benzoylacetonato) (N-methylsalicylaldimino)Ni(II)	16·67 (16·59)	3·73 (3·95)	560	—	3·10
(Benzoylacetonato) (N-ethylsalicylaldimino)Ni(II)	15·55 (15·38)	3·75 (3·66)	560	—	2·92
(Dibenzoylmethanato) (N-methylsalicylaldimino)Cu(II)	15·03 (15·11)	3·15 (3·33)	650	76	1·89
(Dibenzoylmethanato) (N-methylsalicylaldimino)Ni(II)	14·26 (14·12)	3·46 (3·37)	540	—	3·13
(Dibenzoylmethanato) (N-ethylsalicylaldimino)Cu(II)	14·36 (14·17)	3·09 (3·12)	650	72	1·89
(Dibenzoylmethanato) (N-ethylsalicylaldimino)Ni(II)	13·12 (13·23)	3·28 (3·15)	560	—	2·91
(Aquo) [N-(2-hydroxyethylene)salicylaldimino]Cu(II)	25·57 (25·88)	5·58 (5·70)	640	78	1·76
(Benzoylacetonato)[N-(2-hydroxyethylene)salicylaldimino] Ni(II)	14·98 (15·30)	3·42 (3·65)	560	—	2·89
(Dibenzoylmethanato) [N-(2-hydroxyethylene)salicylaldimino]Ni(II)	13·54 (13·17)	3·41 (3·14)	550	—	2·91

Satisfactory C and H analyses were obtained for compound I. Compounds obtained by amine-exchange reactions gave comparable analytical data to the mixed complexes obtained directly.

base[5,6]. Amine-exchange was carried out using excess amine and employing amine as the reaction solvent.

Further, amine-exchange reactions with ethanolamine were also attempted with the present Cu(II) and Ni(II) mixed ligand complexes. In the case of Cu(II) complexes, the aldimine part reacted with ethanolamine to form a tridentate ligand in which OH group of ethanolamine provided the third coordination site. The β-diketone part was, however, removed and the final compound attained tetra coordination through coordination of a water molecule (III).

Similar monomeric complexes of tridentate ligands with solvent molecule occupying the fourth position have been reported earlier[7]. A mechanism similar to that proposed by Chakrovarty *et al.*[8] in the case of Cu(II) complexes of Schiff bases, may be operative here also.

In the case of Ni(II) complexes also the salicylaldehyde moiety condenses with monoethanolamine to form a tridentate ligand. However, the β-diketone part is also retained, though it does not undergo condensation with monoethanolamine. Thus all the four equatorial positions around Ni(II) remain occupied. The -OH group of N-(2-hydroxyethylene) salicylaldimine remains uncoordinated because the Schiff base cannot occupy positions in two different planes[9,10] (IV). The structure however needs confirmation by X-ray study.

Similar reactions of ethanolamine with bis(salicylaldimino)Cu(II) and- Ni(II) have been carried out in our laboratory[11]. It has been observed that in Cu(II) complexes, one of the salicylaldehyde molecule forms a tridentate ligand with monoethanolamine and occupies three positions around the Cu(II) ion; the other salicylaldehyde molecule is removed. In the case of Ni(II) complex, however, both the salicylaldehyde molecules undergo condensation with monoethanolamine.

The reason why the diketone is removed in the case of Cu(II) and retained in the case of Ni(II) may be due to the difference in the stereochemistries of Cu(II) and Ni(II) complexes.

TLC analysis shows the compounds to be pure. The results of elemental analyses agree with the suggested structures (Table 1). All the Schiff base complexes obtained are soluble in common organic solvents. They are found to be non-conducting indicating their non-electrolytic nature.

The Cu(II) complexes are paramagnetic having magnetic moments corresponding to one unpaired electron. The visible spectrum shows a broad band at ~650 nm in agreement with square-planar structure. Ni(II) square-planar complexes are expected to be diamagnetic. The present Ni(II) complexes, however, exhibit paramagnetism. Paramagnetism in Ni(II) complexes of the type (I) and (II) could be attributed to oxygen bridging in these complexes[12-14]. Paramagnetism in compound (IV) is due to the weak coordination of the —OH group of the Schiff base with the metal ion in neighbouring complex molecules. This results in polymerization and formation of distorted octahedral structure in solid state and accounts for paramagnetism. The visible spectra of Ni(II) complexes in chloroform exhibit shoulders around 550 nm. There is no band beyond ~600 nm indicating square-planar structure in solution. This may be due to breaking up of polymerization in the solution.

In the IR spectra of compounds (I) and (II), no bands are observed in the region 3400 cm^{-1} showing thereby that the —OH hydrogen of aldehyde or ketone gets dissociated after complexation. In compound (I), a band around 1625 cm^{-1} corresponds to aldehydic $\nu C = O$, while a band around 1580 cm^{-1} corresponds to $\nu C \underline{\cdots} O$ of the diketone which has delocalized π-electrons. However, in the compound (II) ($R'' = H$) the band around 1625 cm^{-1} disappears and a new band appears around 1600 cm^{-1} which is assigned to $\nu C = N$ of the imine linkage. The band at 1500 cm^{-1} due to $\nu C = O$ of diketone group is, however, retained indicating that it does not undergo condensation. There is also a band around 3300 cm^{-1} corresponding to free $\nu N—H$. This band is, however, absent in case of Schiff base complexes derived from alkylamines.

The IR spectrum of compound (III) exhibits a broad band in the region 3400 cm^{-1} corresponding to OH stretch, confirming the presence of water. There is also a band around 800 cm^{-1} corresponding to the O—H out-of-plane deformation. This indicates the presence of coordinated water. The IR spectra of compound (IV) also exhibits a band around 3400 cm^{-1} corresponding to O—H stretch. This shows that the —OH of the ethanolamine has weak coordination and hence the proton does not get dissociated. Besides the compound also exhibits bands in the regions 1600 cm^{-1} and 1580 cm^{-1} corresponding to $\nu C{=}N$ and $\nu C \underline{\cdots} O$ groups of diketone, respectively, indicating thereby that the diketone does not condense with the amine-group.

Acknowledgement

Thanks are due to Prof. K. N. Trivedi, Head, Department of Chemistry, M.S. University of Baroda, for providing laboratory facilities. Thanks are also due to UGC, New Delhi for providing junior research fellowship to one of the authors (U.D.).

References

1. Doraswamy, Uma & Bhattacharya, P. K., *J. inorg. nucl. Chem.*, **37** (1975), 1665.
2. Lindoy, L. F., *Q. Rev. chem. Soc.*, **25** (1971), 379.
3. West, B. O., *The chemistry of coordination compounds of Schiff base* in *New pathways in inorganic chemistry* edited by E. A. V. Ebsworth, A. G. Maddock & A. G. Sharpe (Cambridge University Press, London), 1968, 307.
4. Busch, D. H., *Adv. Chem. Ser.*, **37** (1963), 1.
5. Verter, H. S. & Frost, A. E., *J. Am. chem. Soc.*, **82** (1960), 85.
6. Olsgwski, E. J. & Martin, D. P., *J. inorg. nucl. Chem.*, **27** (1965), 345.
7. Kubo, M., Kuroda, Y., Kishita, N. & Muto, Y., *Aust. J. Chem.*, **16** (1963), 7.
8. Balundi, R. H. & Chakrovarty, A., *Inorg. Chem.*, **12** (1973), 981.
9. *Progress in inorganic chemistry*, Vol. **7**, edited by F. A. Cotton (Interscience publishers, N.Y.), 1966, 108; 193.
10. *Transition metal chemistry*, Vol. 4, edited by R. L. Carlin (Academic Press, N.Y.), 1968, 289.
11. Kohli, R. K., Mohan Kumar, V. B., Thaker, B. T. & Bhattacharya, P. K., *Bull. chem. Soc. Japan* (in press).
12. Graddon, D. P. & Mockler, G. M., *Aust. J. Chem.*, **20** (1967), 21.
13. Donini, J. C., Hollebone, B. R. & Lever, A. B. P., *J. Am. chem. Soc.*, **93** (1971), 24, 6455.
14. Sacconi, L., Paoletti, P. & Cini, R., *J. Am. chem. Soc.*, **80** (1958), 3583.