Thermochimica Acta, 57 (1982) 369–376
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THERMAL AND OTHER STUDIES OF COPPER AND COBALT COMPLEXES OF SOME LIGANDS CONTAINING THE N–O GROUP

HARBHAJAN SINGH, SMITA SRIVASTAVA and SUMAN MAHESHWARI
Department of Chemistry, University of Delhi, Delhi-110007 (India)

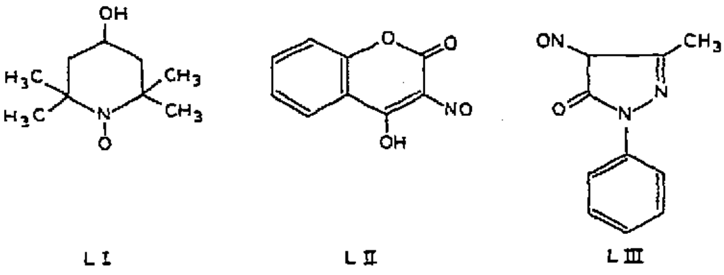
(Received 26 February 1982)

The complexation behaviour of a coordinating group in a different environment is always of interest to inorganic chemists. Studies on the complexes of various N-oxides and nitroso ligands have already been reported by many workers [1]. We now report the complexation behaviour of three ligands viz. 4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl (4-HTMPNO) LI, oximidobenzotetronic acid (OBTA) LII, and 4-nitroso-3-methyl-1-phenyl-2-pyrazoline-5-one (NMPPO) LIII (Fig. 1); each containing the same co-ordinating group, the NO group. The aim is to study the differences in the complexation behaviour of the above ligands as well as in their metal complexes.

EXPERIMENTAL

Chemicals and equipment

4-HTMPNO (LI) and 3-methyl-1-phenyl-2-pyrazoline-5-one were obtained from Aldrich Chemicals Co., U.S.A. A Beckman thermometer was used to determine molecular weight by a cryoscopic method. Thermal studies have been carried out on a Setaram G-70 thermobalance taking 20–30 mg



L I L II L III

Fig. 1. Ligand structures.

0040-6031/82/0000–0000/$02.75

sample size, 7°C min^{-1} heating rate and 10 ml min^{-1} flow rate of oxygen. Infrared spectra in the region 4000–200 cm^{-1} have been recorded in the solid state (cesium iodide pellets) on a Perkin Elmer model 621 IR spectrophotometer.

Synthesis of the ligands

Oximidobenzotetronic acid (LII) was prepared by the nitrosation of 4-hydroxycoumarin under acidic conditions [2] whereas 4-nitroso-3-methyl-1-phenyl-2-pyrazoline-5-one(LIII) was prepared by the addition of 12% cold HCl to an aqueous solution of equimolar amounts of 3-methyl-1-phenyl-2-pyrazoline-5-one and sodium nitrite. The reaction temperature was kept ≤ 5°C. An orange coloured crystalline solid that separated was washed with ice cold water and dried in vacuo over P_4O_{10} (m.p. 152°C). The synthesized ligands were characterized by melting points. molecular weights, IR, NMR and elemental analyses.

Preparation of the complexes of 4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl

Anhydrous metal chlorides were obtained by passing dry HCl gas over heated chlorides. Stoichiometric amounts of the metal (copper or cobalt) salt were mixed with the ligand in THF. The binary complex formed could not be isolated. However, on adding 2 equivalents of dry triethylamine, solid ternary complexes separated. These were filtered and stored over P_4O_{10}.

Preparation of the complexes of oximidobenzotetronic acid (LII) and 4-nitroso-3-methyl-1-phenyl-2-pyrazoline-5-one (LIII)

An aqueous solution of the metal salt was added to an alcoholic solution of the ligand in a stoichiometric ratio of 1:2. The reaction mixture was refluxed for 1–4 h. Upon cooling, solid complexes separated out. The complexes were washed with distilled water followed by cold aqueous ethanol (10%) and dried over P_4O_{10}.

As mentioned above the metal complexes of 4-HTMPNO have been synthesized in a non-aqueous medium whereas complexes of OBTA and NMPPO were synthesized in an aqueous medium due to solubility reasons. It may be mentioned that in each case the prepared complexes do not contain any water of coordination as evidenced by IR and thermal studies.

RESULTS AND DISCUSSIONS

The elemental analyses are presented in Table 1. Molecular weight data suggest the monomeric nature of the complexes. All complexes, except those

TABLE 1

Elemental analyses, molecular weight and infrared spectral data

Complex	C (%)	H (%)	N (%)	M (%)	Molecular weight	νN–O'	νN–O	νC=O	νM=O	ΔνN-O
LI $C_9H_{17}NO_2$	62.9	9.7	7.8		168 (171)	1630				
	(63.0)	(9.9)	(8.2)							
LII $C_9H_5NO_4$	61.5	2.4	7.6		182.1 (163)		1565	1680		
	(61.7)	(2.8)	(7.8)							
LIII $C_9H_9N_3O_2$	56.8	7.5	6.9		187.4 (191)		1550	1675		
	(57.1)	(7.7)	(7.4)							
(a) $[(C_9H_{17}NO_2)_2Cl_2$-	52.9	8.9	7.4	9.3	676.4 (680)	1615			410	15
$(C_6H_{15}N)_2]Cu$	(53.1)	(9.4)	(8.2)	(9.5)						
Cu-4HTMPNO										
(b) $[(C_9H_{17}NO_2)_2Cl_2$-	53.2	9.4	8.1	8.1	670.1 (672)	1610			370	20
$(C_6H_{15}N)_2]Co$	(53.5)	(9.5)	(8.3)	(8.4)						
Co-4HTMPNO										
(c) $[(C_9H_5NO_4)_2]Cu$	52.1	2.2	6.3	15.2	427.2 (429)		1545	1678	435	20
Cu-OBTA	(52.3)	(2.4)	(6.7)	(15.7)						
(d) $[(C_9H_5NO_4)_2]Co$	53.2	2.5	6.6	13.7	418.8 (421)		1535	1680	365	30
Co-OBTA	(53.5)	(2.4)	(6.9)	(14.0)						
(e) $[(C_9H_9N_3O_2)_2(NO_3)_2]Cu$	38.0	2.3	19.3	11.1	567.7 (571)		1523	1660	420	37
Cu-NMPPO	(38.1)	(2.5)	(19.7)	(11.4)						
(f) $(C_9H_9N_3O_2)_2(NO_3)_2Co$	38.4	2.2	19.8	10.2	561.5 (563)		1515	1650	380	35
Co-NMPPO	(38.6)	(2.4)	(20.0)	(10.4)						

TABLE 2

Kinetic parameters and electronic spectral data

Complex	Dec. temp. (°C)		% wt. loss		Activation energy (cal mole^{-1})		λ_{max} (cm^{-1})	Transitions
	Step I	Step II	Step I	Step II	Step I	Step II		
(a) Cu-4HTMPNO	98		87.2 (88.0)		12560		13800	${}^2E_g \rightarrow {}^2T_{2g}(\nu_1)$
(b) Co-4HTMPNO	110		89.0 (89.4)		13475		8320 26470	${}^4T_{1g} \xrightarrow[\text{CT}]{} u4T_{2g}$
(c) Cu-OBTA	100	200	40.6 (40.9)	80 (81.7)	16580	10835	14250 19380	${}^2T_2 \xrightarrow[\text{CT}]{} {}^2E$
(d) Co-OBTA	135	170	40.8 (41.5)	83.1 (82.3)	24800	13474	8420, 18020, 21850, 24670	${}^4T_{1g} \rightarrow {}^4T_{2g}$ ${}^4T_{1g} \xrightarrow[\text{CT}]{} {}^4A_{2g}$
(e) Cu-NMPPO	105	170	35.0 (38.6)	85.0 (85.7)	20880	15560	14600 27320	${}^2E_g \xrightarrow[\text{CT}]{} {}^2T_{2g}$
(f) Co-NMPPO	128	200	38.0 (39.3)	(86.9)	26600	16720	841, 17870, 21600	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$ ${}^4T_{1g} \rightarrow {}^4T_{1g}(F)$

of 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl are soluble in common organic solvents.

Thermal studies

The use of thermogravimetric data to evaluate kinetic parameters of solid state reactions involving weight loss had been investigated by a number of workers [3,4]. We have followed the method of Coats and Redfern [5]. Kinetic parameters of each decomposition step have been calculated from TG curves and presented in Table 2. The probability that a molecule possesses energy in excess of an amount E per mole, at a temperature T is related to the Boltzmann factor $e^{-E/RT}$, where R is the molar gas constant. The reaction rate is dependent upon the product of A, which is the frequency factor and $e^{-E/RT}$. Thus the decomposition equation of a first order reaction of the type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$ will be

$$K = A\, e^{-E/RT}$$

For a first order reaction i.e. $n = 1$, this equation takes the form

$$-\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = A\ e^{-E/RT}$$

However, when $n \neq 1$, this equation becomes

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = A\ e^{-E/RT}$$

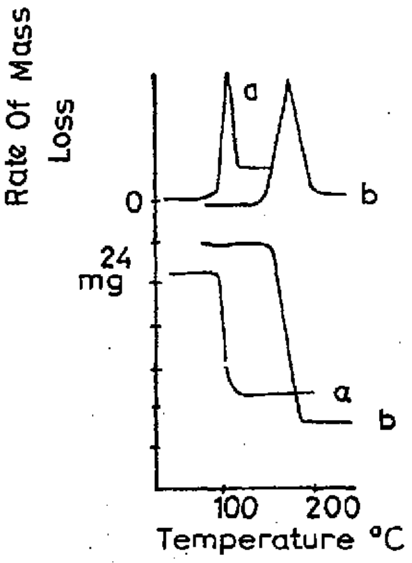


Fig. 2. TG and DTG curves for (a) Cu-4HTMPNO and (b) Co-4HTMPNO.

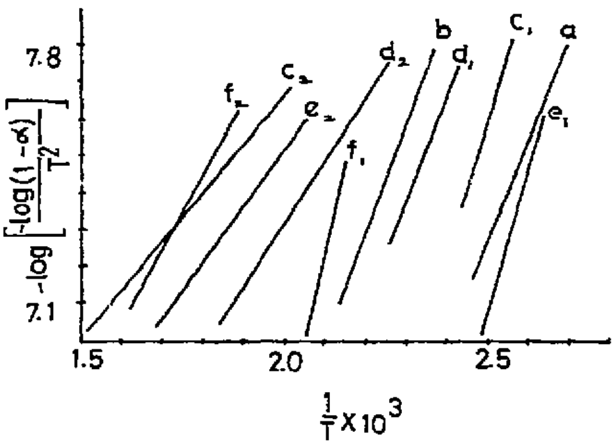


Fig. 3. Coats and Redferns linearization curves of complexes (a)–(f).

From the plot of the LHS vs. $1/T$ the order of reaction has been evaluated.

The TG/DTG curves of complexes (a) and (b), Fig. 2, consist of only one decomposition step which begins at ≥ 100°C. A fast rate of weight loss is observed and the complexes decompose explosively. At temperature ~ 450°C the stable metallic oxide is formed. The plot of $-\log\{-\log(1-\alpha)/T^2\}$ vs. $1/T$ results in a straight line of slope $= -E/2.303\ R$ (Fig. 3). The order of the reaction has been found to be one in both cases. The apparent activation energy calculated for the solid state decomposition reaction

$$[M(LI)_2(Et_3N)_2Cl_2] \xrightarrow{O_2} MO$$

where M = Cu or Co, is given in Table 2.

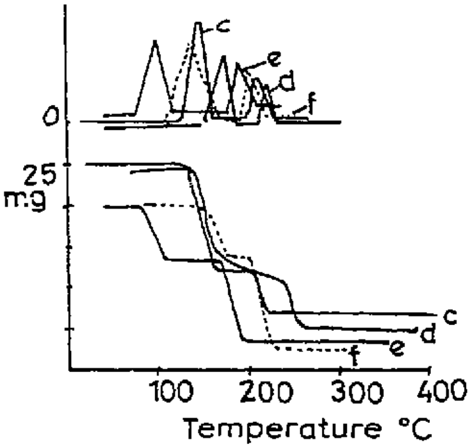


Fig. 4. TG and DTG curves of (c) Cu-OBTA, (d) Co-OBTA, (e) Cu-NMPPO and (f) Co-NMPPO.

Thermal decomposition curves of complexes (c), (d), (e) and (f) in Fig. 4 are identical to each other showing two decomposition steps.

The first decomposition step begins only at $\geqslant 110°\mathrm{C}$ indicating the absence of any water molecule. The decrease in weight with increase in temperature corresponds to the formation of a 1 : 1 complex consequent to the loss of one ligand molecule. These intermediates formed after the first weight loss have been confirmed on the basis of their elemental analyses and infrared spectra. Further heating then results in further weight loss with the ultimate formation of a thermally stable oxide. The overall reaction is summarized as

$$[\mathrm{M(HLII)_2}] \xrightarrow{\mathrm{O_2}} \mathrm{MLII} \rightarrow \mathrm{MO} \quad \text{(for (c) and (d))}$$

$$[\mathrm{M(LIII)_2(NO_3)_2}] \xrightarrow{\mathrm{O_2}} \mathrm{MLIII} \rightarrow \mathrm{MO} \quad \text{(for (e) and (f))}$$

The thermal decomposition range and the calculated apparent activation energy have been presented in Table 2.

Infrared spectral studies

The spectra of all the complexes indicate that the N–O group is involved in bond formation. This is supported by the observed shift in the ν(N–O) frequency. The absence of a band at 3500 $\mathrm{cm^{-1}}$ due to an –OH group in the spectra of complexes (c) and (d) indicates the involvement of the hydroxyl group as well. New bands are observed in the spectra of all the complexes characteristic of M–O and M–N bonds [7]. IR Data is presented in Table 1.

Visible spectral studies

Copper in the complexes of LI and LIII has a co-ordination number of 6 and the expected geometry is a distorted octahedron. The ground state of octahedrally coordinated Cu(II) is $^2E_g(t_{2g})^6(e_g)^3$. The only excited state should then be $^2T_{2g}(t_{2g})^5(e_g)^4$. We observe only one sharp band at 13500–14500 $\mathrm{cm^{-1}}$ due to *d–d* transition $^2E_g \rightarrow {}^2T_{2g}(\nu_1)$. In the Cu–LII complex, one band observed at 14250 $\mathrm{cm^{-1}}$ is assigned to $^2T_2 \rightarrow {}^2E$ in a tetrahedral field. In the Co–LI complex one band is observed at 8320 $\mathrm{cm^{-1}}$ whereas in Co–LII and Co–LIII more than one band is observed at 840–24670 $\mathrm{cm^{-1}}$. Transitions assigned to these have been presented in Table 2. Charge transfer bands are observed in the tetrahedrally co-ordinated cobalt complex of LII.

CONCLUSION

The above results suggest involvement of the NO group in bond formation in each case. In the complexes of LII and LIII a chelate ring is formed imparting a greater stability to the complexes in comparison with co-ordinate bond formation in the case of free radical (LI) complexes. This order of stability is also observed in the calculated activation energies and it may be inferred that 4-nitroso-3-methyl-1-phenyl-2-pyrazoline-5-one forms the most stable complexes. This view is also supported by the observed $\Delta\nu(N-O)$ shifts.

ACKNOWLEDGEMENT

The authors wish to thank U.G.C. and B.P. R. and D., New Delhi for financial assistance to S.S. and S.M., respectively.

REFERENCES

1 N.M. Karyannis, L.L. Pyttewcki and C.M. Mikulski, Coord. Chem. Rev., 11 (1973) 93.
2 A.N. Bhat, Ph.D. Thesis, University of Delhi, (1962) p. 109.
3 E.S. Freeman and B. Caroll, J Phys. Chem., 62 (1958) 394.
4 A. Berlin and R.J. Robinson, Anal. Chim. Acta, 27 (1962) 50.
5 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
6 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier Publishing Co., London, 1963.
7 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Co-ordination Compounds, John Wiley and Sons, New York, 1978.