Magnetic and spectral studies on 3d-metal complexes of acetone(N-isopropylidene)tyrosyl hydrazone

T R RAO*, MAMTA SAHAY and R C AGGARWAL

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India

Abstract. Acetone(N-isopropylidene)tyrosyl hydrazone, $HO\text{-}C_6H_4\text{-}CH_2\text{-}CH(N=CMe_2)\text{-}CONHN=CMe_2$ (ATH), has been found to form adducts of the type M (ATH) $Cl_2 \cdot nH_2O$ [M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); n = 0, 1 or 2] and deprotonated complexes of the type M'(ATH-2H)$\cdot 3H_2O$ [M' = Co(II), Ni(II) and Cu(II)]. Molar conductance studies in 0·001 M DMSO solution have indicated the non-ionic nature of the complexes. High-spin octahedral geometry for Mn(II) and Ni(II) complexes and tetrahedral geometry for Co(II) adduct have been proposed on the basis of magnetic and/or electronic spectral studies. IR spectra suggest neutral bidentate and dinegative tridentate behaviour of the ligand in the adducts and deprotonated complexes respectively. ESR spectra of Cu(II) complexes indicate zero-field splitting of $Cu(ATH)Cl_2 \cdot H_2O$ and metal-metal interaction in both the complexes.

Keywords. Acetone(N-isopropylidene)tyrosyl hydrazone; 3d-metal complexes; deprotonated complexes; neutral bidentate behaviour; dinegative tridentate behaviour.

1. Introduction

In view of a current upsurge of interest in the transition metal complexes of biologically active ligands, particularly of amino acids and their derivatives (McAuliffe and Murray 1973; Bunel *et al* 1981; Bontchev *et al* 1981; Antolini *et al* 1982), we recently initiated in this laboratory an investigation on the coordination properties of amino acid hydrazides and their derivatives; in this frame work we have previously reported the synthesis and structural studies of first row transition metal complexes of 1-tyrosine hydrazide and (N-benzoyl)glycine hydrazide (Rao *et al* 1984; Rao *et al* 1985).

In the present paper we describe the results of our investigations on the synthesis and structural studies of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of acetone(N-isopropylidene)tyrosyl hydrazone (ATH).

2. Experimental

2.1 *Starting materials*

All the metal chlorides used in this study were of BDH, AR grade. 1-Tyrosine hydrazide, obtained from M/s Sigma Chemical Company, USA, was used as such. Acetone(N-isopropylidene)tyrosyl hydrazone was prepared by refluxing 1-tyrosine hydrazide in

---

* To whom all correspondence should be addressed.

excess of acetone for about 8 hr. The white micro-crystalline powder obtained on cooling the reaction mixture to room temperature was separated by filtration, washed with acetone and ether and recrystallized from acetone, m.p. 145°C. Analysis: calcd. for $C_{15}H_{21}N_3O_2$: C, 65·47; H, 7·63; N, 15·26; N_2H_4, 11·63%. Found: C, 65·23; H, 7·59; N, 15·20; N_2H_4, 11·58%.

2.2   *Preparation of the complexes*

Complexes of the general formula M (ATH)$Cl_2 \cdot n H_2O$ [M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were prepared by adding a solution of $\approx$ 2·5 mmol of ATH in acetone to a solution of the appropriate metal chloride ($\approx$ 2·5 mmol) in an acetone-ethanol mixed solvent. Addition of a few drops of dil. HCl to the above metal-ligand solution resulted in the formation of a gummy solid in each case, which on maceration with acetonitrile, yielded the micro-crystalline complex. The complexes, thus obtained, were filtered, washed with acetone and ether and dried in a desiccator.

Complexes of the general formula M'(ATH-2H)$\cdot 3H_2O$ [M' = Co(II), Ni(II) and Cu(II)] were synthesized as follows: To an aqueous solution of ATH ammonium hydroxide was added drop by drop until its pH rose to $\approx$ 6·5 followed by the addition of an aqueous solution of the appropriate metal chloride in equimolar ratio. The complexes precipitated immediately and were digested on a water bath for $\approx$ 5 min, filtered, washed successively with water, ethanol and ether and dried at room temperature.

2.3   *Analyses of the complexes*

The metal and the halide were analysed gravimetrically. Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. The water-content of the complexes was determined from the loss of weight suffered by them on heating in the temperature range 90–200°C. C, H and N were microanalysed. The analytical data are given in table 1.

2.4   *Physical measurements*

Details of the equipment used for various physico-chemical studies were the same as reported earlier (Rao *et al* 1984; Rao *et al* 1985). Effective magnetic moments are included in table 1 while the spectral data are given in tables 2 and 3.

3.   **Results and discussion**

The analytical data in table 1 show that the metal-ligand interaction gives rise to the formation of two types of complexes, viz, the adducts and the neutral or deprotonated complexes in weakly acidic and alkaline media respectively. Based on the formation of the deprotonated complexes, an amide $\rightleftharpoons$ imidol tautomerism of ATH as a function of

CMe₂ ... high pH ... C Me₂ ... low pH ...
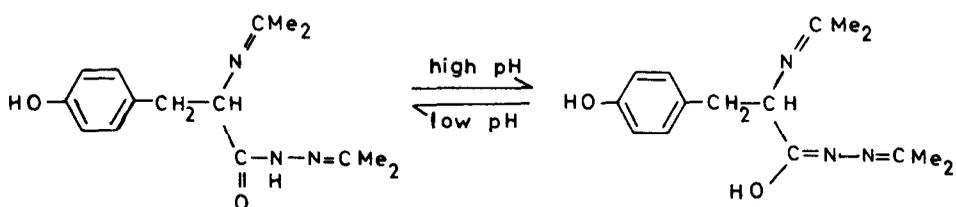
pH may be formulated as shown above: It appears from the dinegative behaviour of the ligand in the neutral complexes that besides the deprotonation of the imidol group, elimination of the phenolic proton also occurs as that reported for tyrosine (Chow and McAuliffe 1975).

The complexes are non-hygroscopic and fairly stable under ordinary atmospheric conditions. With a few exceptions all of them are insoluble in water and common organic solvents but are soluble in DMF and DMSO. All the adducts are found to melt at specific temperatures as given in table 1 while the deprotonated complexes are non-melting below 300°C. The insolubility in common organic solvents and the non-melting nature of the deprotonated complexes suggest a polymeric nature. The molar conductance values of the complexes in 0·001 M DMSO solutions lie in the range $0·47-7·1 \ \text{ohm}^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ indicating their non-ionic nature (Geary 1971).

3.1 *Magnetic moments*

The room temperature magnetic moments indicate a spin-free tetrahedral or octahedral geometry for the Mn (II) complex and octahedral geometry for Ni (II) complexes (Figgis and Lewis 1964). The μ_{eff} value obtained for Co(ATH)Cl₂ is typical of a tetrahedral stereochemistry (Figgis and Lewis 1964) while the subnormal magnetic moment (3·23 BM) of Co(ATH-2H)·3H₂O may be explained by assuming a polymeric formulation with magnetic exchange (Williams *et al* 1967; Henke and Kremer 1982). The magnetic moments of Cu (II) complexes which are slightly lower than the spin-only value, reflect the presence of a weak metal-metal interaction (Kato *et al* 1964).

3.2 *Electronic spectra*

The electronic spectra of the complexes have been recorded as nujol mull; the band maxima, their assignments and the calculated ligand-field parameters are given in table 2. The data indicate a tetrahedral geometry for Co(ATH)Cl₂ (Cotton *et al* 1961) and an octahedral environment around Ni (II) in its complexes (Lever 1968). The band positions of Cu (II) complexes suggest a pseudo-octahedral geometry (Lever 1968). These assignments are in accord with the conclusions drawn earlier based on the room temperature magnetic moments of the complexes.

3.3 ESR *spectra*

The room temperature ESR spectra of both Cu(ATH)Cl₂ · H₂O and Cu(ATH-2H)·3H₂O are isotropic in nature; however, their DMF-glass spectra are well resolved with substantial superhyperfine structure in the $g_\perp$ region (figure 1). The spectral parameters given in table 3 show the trend $g_\parallel > g_\perp > 2·0023$, consistent with a $d_{x^2-y^2}$ ground state

Table 1. Elemental analysis and general behaviour of ATH complexes.

Complex	Colour	Nature	M.P. (°C)	Analysis found (calcd.) %						μ_{eff} (BM)
				M	C	H	N	Cl	N_2H_4	
$Mn(ATH)Cl_2 \cdot 2H_2O$	Light yellow	Microcrystalline	195	12·60 (12·57)	41·04 (41·20)	5·67 (5·72)	9·54 (9·61)	16·44 (16·32)	7·48 (7·32)	6·15
$Co(ATH)Cl_2$	Blue	Microcrystalline	180	14·48 (14·55)	44·31 (44·46)	5·22 (5·18)	10·26 (10·37)	17·31 (17·51)	7·88 (7·90)	4·30
$Ni(ATH)Cl_2 \cdot 2H_2O$	Green	Microcrystalline	277d	13·31 (13·32)	40·72 (40·85)	5·62 (5·67)	9·48 (9·53)	16·14 (16·09)	7·27 (7·26)	2·80
$Cu(ATH)Cl_2 \cdot H_2O$	Green	Microcrystalline	148	14·78 (14·87)	42·04 (42·10)	5·43 (5·38)	9·77 (9·82)	16·48 (16·59)	—	1·63
$Zn(ATH)Cl_2 \cdot 2H_2O$	Yellow	Microcrystalline	240	14·66 (14·62)	40·30 (40·24)	5·39 (5·59)	9·28 (9·39)	15·63 (15·85)	7·40 (7·15)	Dia-mag.
$Co(ATH-2H) \cdot 3H_2O$	Brown	Noncrystalline	> 300	15·21 (15·27)	46·61 (46·64)	6·51 (6·48)	10·86 (10·88)	—	8·42 (8·29)	3·23
$Ni(ATH-2H) \cdot 3H_2O$	Light pink	Noncrystalline	> 300	15·29 (15·22)	46·72 (46·67)	6·40 (6·48)	10·72 (10·88)	—	8·58 (8·30)	2·76
$Cu(ATH-2H) \cdot 3H_2O$	Blue	Noncrystalline	185d	16·17 (16·27)	46·11 (46·08)	6·31 (6·40)	10·77 (10·75)	—	—	1·54

d Decomposition temperature.

Table 2. Electronic spectral data and various ligand-field parameters of ATH complexes.

Complex	Band maxima (cm^{-1})	Assignments	Dq (cm^{-1})	B' (cm^{-1})	β	$\beta°$ (%)	LFSE (kJ/mole)
Co(ATH)Cl$_2$	6250, 15380	$^4A_2 \rightarrow {}^4T_1(F), {}^4T_1(P)$	360	721	0·75	25	52
Ni(ATH)Cl$_2$·2H$_2$O	9091, 13990, 22220	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F), {}^3T_{1g}(P)$	909	596	0·56	44	130
Cu(ATH)Cl$_2$·H$_2$O	15270	$^2E_g \rightarrow {}^2T_{2g}$	1527	—	—	—	109
Co(ATH-2H)·3H$_2$O	8335, 16000	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4T_{1g}(P)$	922	577	0·60	40	88
Ni(ATH-2H)·3H$_2$O	10150, 15620, 19050	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F), {}^3T_{1g}(P)$	1015	634	0·60	40	146
Cu(ATH-2H)·3H$_2$O	15500	$^2E_g \rightarrow {}^2T_{2g}$	1550	—	—	—	110

Table 3. ESR parameters of copper complexes of ATH.

Complex	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A_{iso}^{a}	$A_{\parallel}^{a}$	$A_{\perp}^{a}$	G	$D_{\parallel}$ (gauss)
$Cu(ATH)Cl_2 \cdot H_2O$	2·129	2·241	2·072	50·66	113·6	19·16	3·34	40·0
$Cu(ATH-2H) \cdot 3H_2O$	2·122	2·242	2·062	72·68	168·2	24·91	3·90	—

[a] Units, $\times 10^{-4}$ cm^{-1}.

(Goodman and Raynor 1970). An elongated tetragonal-octahedral stereochemistry is proposed for both the complexes in consistence with their lowest g values greater than 2·04 (Bertini *et al* 1979). The identical $g_{\parallel}$ values observed for the complexes indicate a similar type of bonding arising from a $CuNO_3$ chromophore in each of the complexes Massacesi *et al* 1978 & 1979).

The spectrum of $Cu(ATH)Cl_2 \cdot H_2O$ seems to be more complicated due to the presence of zero-field splitting appropriate for a triplet state. Both the overlapping seven-line sets have been identified in the parallel region of the DMF-glass spectrum and its analysis gives $D_{\parallel} \simeq 40G$. Besides, as a consequence of the exchange interaction, the $A_{\parallel}$ value comes to be $113·6 \times 10^{-4}$ cm^{-1} which is almost half of that for $S = 1/2$ species (Hasty *et al* 1978). The presence of significant exchange interaction in these complexes is also indicated by the fact that $G < 4·0$ (Hathaway and Billing 1970), where $G = g_{\parallel} - 2)/(g_{\perp} - 2)$. Further, the spectra show intense peaks centered at $1610 G$ ($g = 3·98$) and $1700 G$ ($g = 3·82$) in the $\Delta M_s = 2$ region of the $Cu(ATH)Cl_2 \cdot H_2O$ and $Cu(ATH-2H) \cdot 3H_2O$ respectively suggesting the presence of metal-metal interaction (Smith and Pilbrow 1974).

3.4 Infrared spectra

The bonding sites of ATH involved in the adducts as well as the neutral complexes have been determined by a careful comparison of the IR spectra of the complexes with the spectrum of the ligand. ATH shows a band at 1670 cm^{-1} in the solid state and at 1690 cm^{-1} in acetonitrile solution due to $>C=O$ stretching frequency indicating the involvement of the $>C=O$ group in hydrogen bonding in the solid state. To minimise the effect of hydrogen bonding, the spectra of the complexes have been compared with the solution spectrum of the ligand. As the spectra of the complexes in the NH stretching region are very complicated due to the overlap of v(NH) and v(OH) absorptions resulting into a broad band, we have refrained from drawing any conclusion from the bands appearing in this region. The bands arising in the solution spectrum of the ligand at 1690, 1610, 1510, 1320 and 1035 cm^{-1} are assigned to amide I, v(C=N), amide II, amide III and v(N–N) modes respectively (Nagano *et al* 1964); the corresponding bands in the spectra of the adducts are observed in the 1665–1625, 1600–1590, 1490–1480, 1340–1335 and 1090–1080 cm^{-1} regions. Thus, a negative shift in the amide I and amide II bands and a positive shift in the amide III band observed in the spectra of the adducts indicate bonding through the oxygen of the amide group (Nagano *et al* 1964). However, the absence of amide I, II and III bands and the presence of new bands characteristic of v (NCO^{-}) in the 1515–1510 and 1395–1385 cm^{-1} regions
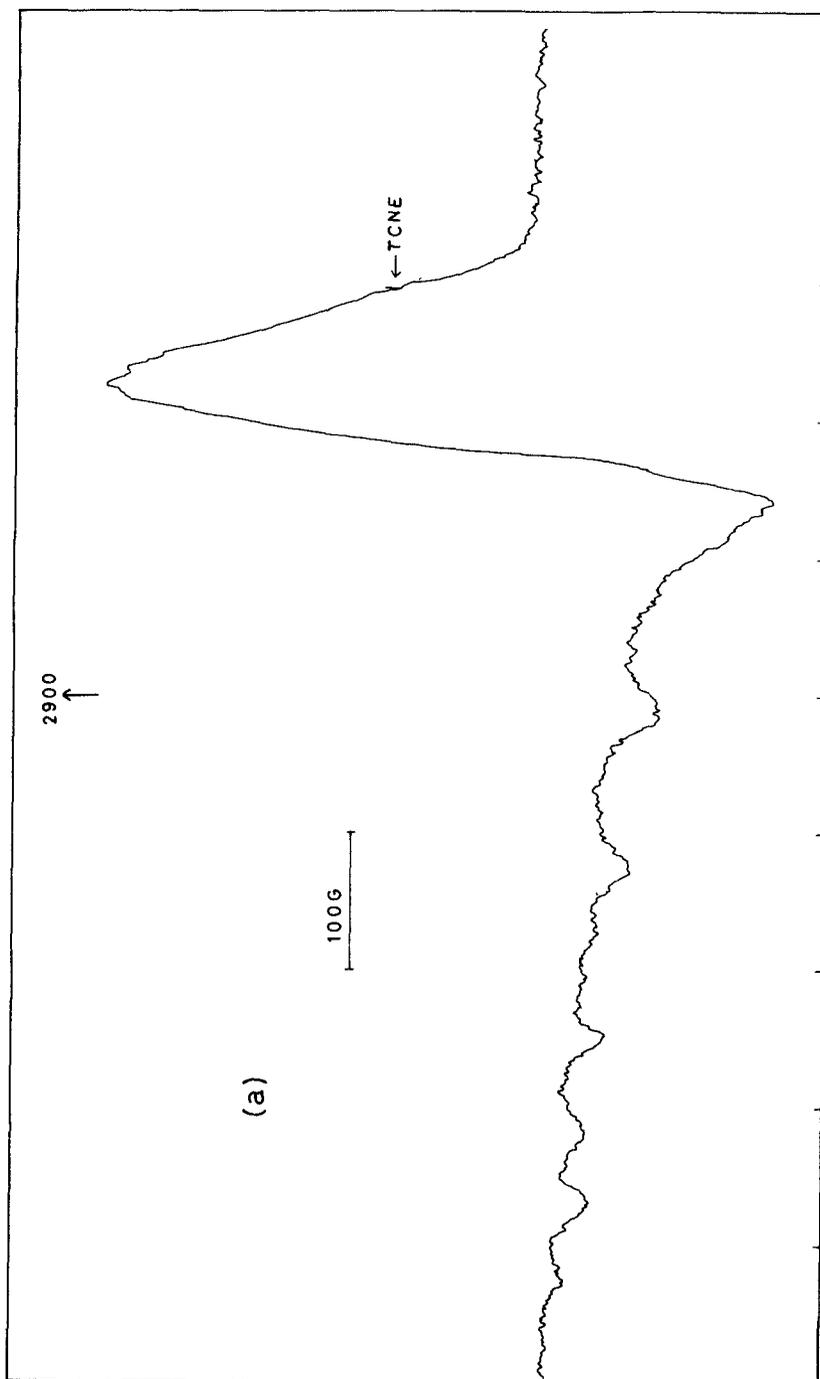
(a)

2900

100 G

←TCNE
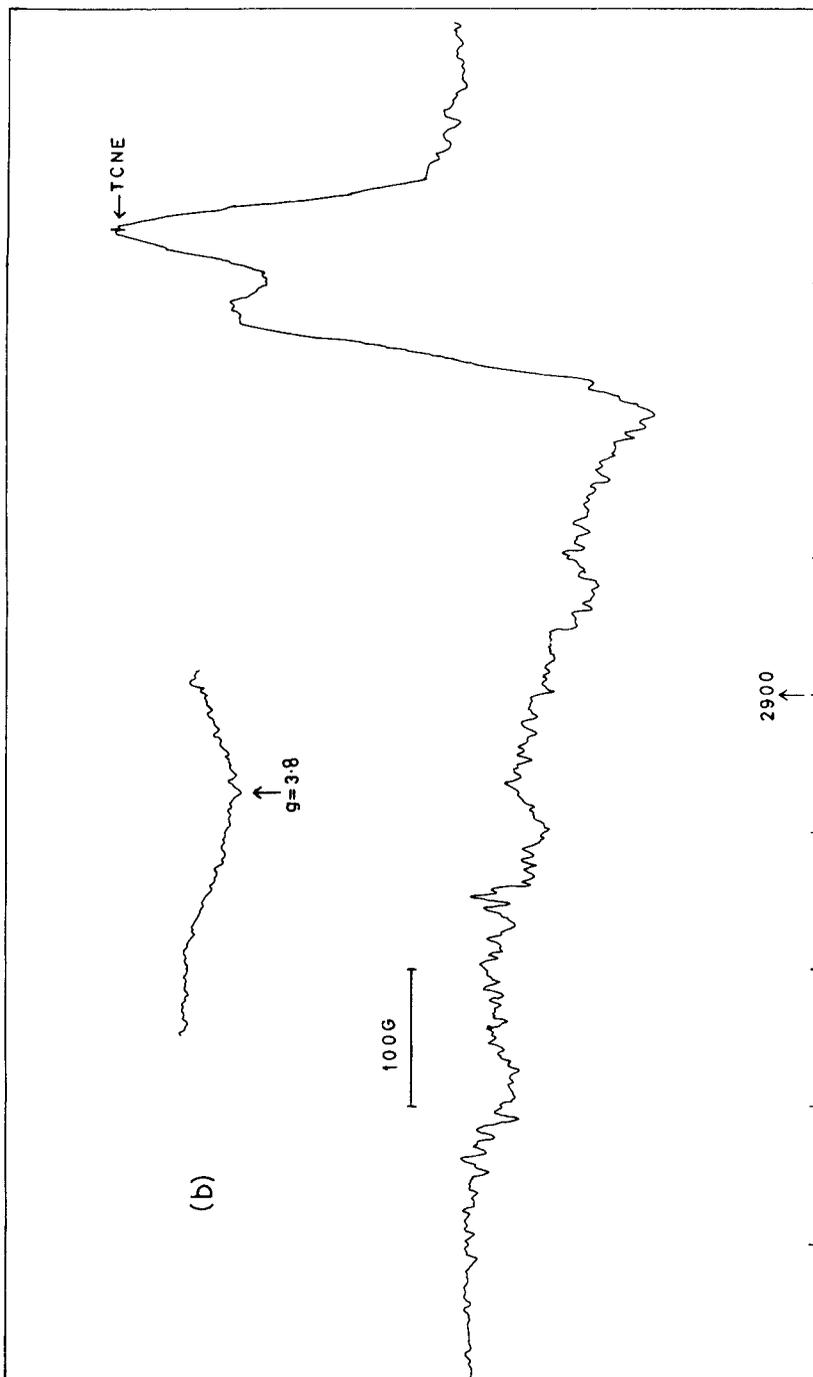
Figure 1. a

Figure 1. ESR spectrum of **a.** Cu(ATH)Cl$_2$ · H$_2$O, and **b.** Cu(ATH-2H) · 3H$_2$O, in DMF at liquid nitrogen temperature.

in the spectra of the deprotonated complexes show the destruction of the keto group through amide ⇌ imidol tautomerism (Rao 1963). Further, a negative shift in the position of the azomethine group of the hydrazone moiety in the spectra of all the complexes compared to that of the ligand indicates coordination through the azomethine nitrogen (Rao 1963); coordination through this group is further substantiated by the observed positive shift of the order $50-60$ cm^{-1} in the v(N–N) mode in all the complexes (Braibanti *et al* 1968). The bands appearing in the free ligand at 1235 and 620 cm^{-1} assigned to the in-plane and out-of-plane deformation modes of the phenolic-OH group (Inomata *et al* 1974) remain almost unaltered in the spectra of all the adducts while both the bands disappear in the deprotonated complexes indicating the non-involvement of the phenolic-OH group in the former complexes and deprotonation of the same and subsequent coordination in the latter (Inomata *et al* 1974). The non-ligand bands appearing in the $480-400$ and $340-290$ cm^{-1} region of the spectra of the adducts as well as the neutral complexes may be tentatively assigned to $v(M$–N) and $v(M$–O) modes respectively (Nakamoto 1978).

In order to make more unequivocal assignments of the band positions due to $v(M$–O) and $v(M$–N) modes, far IR spectra of two representative complexes, Cu(ATH)Cl$_2 \cdot$ H$_2$O and Cu(ATH-2H)$\cdot$ 3H$_2$O were recorded in the region $650-100$ cm^{-1}. The spectrum of Cu(ATH)Cl$_2 \cdot$ H$_2$O shows two strong peaks at 443 and 326 cm^{-1} while that of Cu(ATH-2H)$\cdot$ 3H$_2$O appear at 460 and 340 cm^{-1}; the former peak in each case may be assigned to $v(M$–N) while the latter to $v(M$–O) mode (Herlinger and Long 1970; Kincaid and Nakamoto 1976).
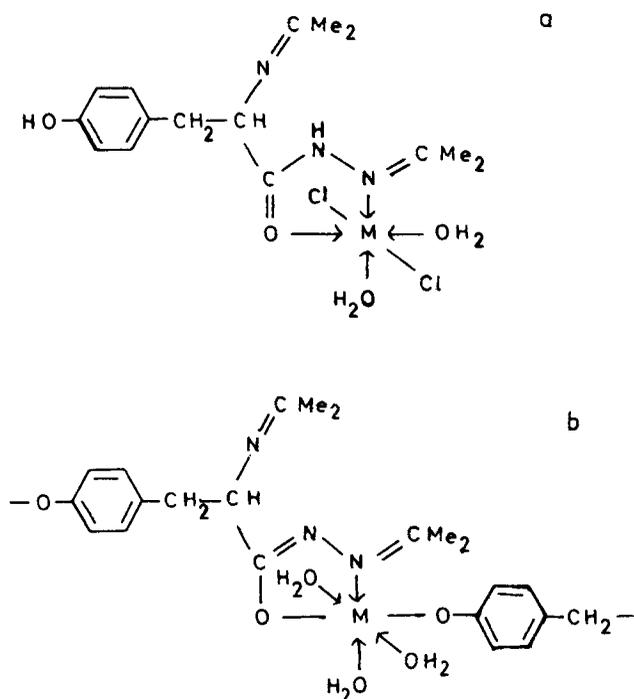

Figure 2. Structure of **a**. M (ATH)Cl$_2 \cdot$ 2H$_2$O[M = Mn(II), Ni(II) and Zn(II)], and **b**. M (ATH-2H)$\cdot$ 3H$_2$O [M = Co(II), Ni(II) and Cu(II)].

Based on the chemical composition and various physico-chemical studies, structures shown in figure 2a and b may be tentatively proposed for the ATH complexes.

Acknowledgements

References

Antolini L, Menabue L, Prampolini P and Saladini M 1982 *Inorg. Chim. Acta* **66** 19
Bertini I, Gatteschi D and Scozzafava A 1979 *Coord. Chem. Rev.* **29** 67
Bontchev P R, Boneva M, Mitewa M, Mehandjeiv D and Golovinsky E 1981 *J. Inorg. Nucl. Chem.* **43** 1363
Braibanti A, Dallavalle F, Pellinghelli M A and Leporati E 1968 *Inorg. Chem.* **7** 1430
Bunel S, Ibarra C, Rodriguez M, Urbina A and Bunton C A 1981 *J. Inorg. Nucl. Chem.* **43** 967
Chow S T and McAuliffe 1975 in *Progress in inorganic chemistry* (ed.) S J Lippard (New York: John Wiley and Sons) Vol. 19, p. 56
Cotton F A, Goodgame D M L and Goodgame M 1961 *J. Am. Chem. Soc.* **83** 4690
Figgis B N and Lewis J 1964 in *Progress in inorganic chemistry* (ed.) S J Lippard (New York: John Wiley and Sons) Vol. 6, p. 197
Geary W J 1971 *Coord. Chem. Rev.* **7** 81
Goodman B A and Raynor J B 1970 *Adv. Inorg. Chem. Radiochem.* **13** 135
Hasty E F, Wilson L J and Hendrickson D N 1978 *Inorg. Chem.* **17** 1836
Hathaway B J and Billing D E 1970 *Coord. Chem. Rev.* **5** 143
Henke W and Kremer S 1982 *Inorg. Chim. Acta* **65** L115
Herlinger A W and Long T V 1970 *J. Am. Chem. Soc.* **92** 6481
Inomata Y, Inomata T and Moriwaki T 1974 *Bull. Chem. Soc. (Jpn)* **47** 818
Kato M, Jonassen H B and Fanning J C 1964 *Chem. Rev.* **64** 99
Kincaid J R and Nakamoto K 1976 *Spectrochim. Acta* **A32** 277
Lever A B P 1968 *Inorganic electronic spectroscopy* (Amsterdam: Elsevier)
Massacesi M, Ponticelli G, Buddha A V and Krishnan V G 1978 *J. Mol. Struct.* **48** 55
Massacesi M, Ponticelli G, Buddha A V and Krishnan V G 1979 *J. Mol. Struct.* **51** 27
McAuliffe C A and Murray S G 1973 *Inorg. Chim. Acta* **7** 171
Nagano K, Kinoshita H and Hirakawa A 1964 *Chem. Pharm. Bull.* **12** 1198
Nakamoto K 1978 in *Infrared and Raman spectra of inorganic and coordination compounds* 3rd Ed (New York: Wiley Interscience) pp. 199, 228
Rao C N R 1963 *Chemical applications of infrared spectroscopy* (New York: Academic Press) p. 265
Rao T R, Sahay M and Aggarwal R C 1984 *Indian J. Chem. (A)*23 214
Rao T R, Sahay M and Aggarwal R C 1985 *Synth. React. Inorg. Met.-Org. Chem.* **15** 209
Smith T D and Pilbrow J R 1974 *Coord. Chem. Rev.* **13** 173
Williams D L, Smith D W and Staufer R C 1967 *Inorg. Chem.* **6** 590