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Characterisation of Some Metal Complexes of Thiazolidine-4-Carboxylic Acid

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A series of metal complexes of thiazolidine-4-carboxylic acid (prepared by Ratner and Clarke procedure) were synthesised in neutral or in alkaline medium at pH 8.0. The stoichiometries of the metal compounds were established on the basis of elemental analysis and metal content determination. Magnetic measurements have shown that iron forms ferromagnetic compound, Cobalt(II) high spin octahedral complex, nickel a tetrahedral surrounded with octahedral species and copper a dimer on account of sulphur exchange mechanism. The IR spectra on interpretation have shown that metals are bonded at N of NH group and oxygen of COO group of the ligand.

INTRODUCTION

In recent years the binding of sulphur containing amino acids and their derivatives of transition metal ions have aroused considerable interest due to potential use of these organo compounds in metal chelation therapy.[1] Among the sulphur containing amino acids, cysteine derivatives, penicillamine and N-acetyl penicillamine have been clinically used for the treatment of mercury and cadmium poisoning.[2–5] Thiazolidine-4-carboxylic acid and its salts have been used in the treatment of liver diseases (Wilson disease)[6]. Inspired by this growing interest in the complexing behaviour of sulphur containing amino acids and their probable therapeutic use, biologically important sulphur containing amino acid *i.e.* thiazolidine-4-carboxylic acid was taken up for its complexing behaviour with first row transition metal ions.

EXPERIMENTAL

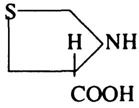
Preparation of ligand thiazolidine-4-carboxylic acid (AH_2) was carried out by Ratner and Clarke[7] procedure. Metal salts of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Hg(II) of AR quality were used for the preparation of metal complexes.

The complexes of these metals with the ligand were prepared either in neutral medium or in slightly alkaline medium pH at *ca.* 8.0. The stoichiometries of the prepared compounds were established on the basis of elemental analysis (Table 1).

TABLE-1

ANALYTICAL DATA OF LIGAND (AH_2) AND METAL COMPLEXES

AH_2 =



THIAZOLIDINE-4-CARBOXYLIC ACID

S. No.	Complexes	Molecular weight	Found (%)				
			C	H	N	S	Metal
1.	$FeAH\cdot Cl_2$	258.85	18.60	2.19	5.50	12.41	21.47
2.	$Co(AH)_2\cdot 2H_2O$	358.93	26.68	4.50	7.92	17.79	16.32
3.	$Ni(AH)_2\cdot 4H_2O$	394.71	24.18	5.18	1.10	16.28	14.81
4.	$CuA\cdot 2H_2O$	230.54	21.00	4.00	6.10	13.91	27.63
5.	$Zn(AH)Cl\cdot 2H_2O$	250.87	19.20	3.21	5.52	12.83	26.11
6.	$Ag(AH)_2(AH)$	372.87	25.18	3.49	7.48	17.20	28.87
7.	$Cd(AH)_2\cdot 2H_2O$	412.40	23.21	3.91	6.81	15.62	27.25
8.	Hg(A)	331.59	14.39	1.48	4.21	9.60	60.62

Chlorine % of compound No. 1—27.41, Compound No. 5—14.16

Magnetic susceptibilities of the complexes were evaluated by Gouy's procedure. Iron forms $Fe(AH)Cl_2$ complex of ferromagnetic nature. The ferromagnetism of the compound is attributed to antiferromagnetic alignment of spins on sublattices canted to be of the order of the ratio of the anisotropic to the isotropic interactions without any external field and that only two sublattices are involved in canting.

The room temperature magnetic moment 5.19 B.M. for cobalt complex lies well within 4.65–5.2 B.M.[8] specified for high spin octahedral Co(II) compounds. The observed magnetic moment of nickel(II) complex 3.40 for 112 : 2, metal : thioligand : water, as is independent of field strength, has been interpreted free from any ferromagnetic impurities.[9] The value is higher than the spin only moment value 2.83 B.M. for two unpaired electrons and may be classed either as four coordinated tetrahedral or six coordinated octahedral complex; however, the effect of temperature on the observed moment to classify the compound for any particular geometry could not be carried out.

The magnetic moment value of copper compound is found to be 1.14 B.M. has been explained on account of super exchange mechanism due to dimeric nature. The mechanism is possibly operative either through pathway analogous to other dimeric carboxylic acid copper complexes[10] or through ring sulphur rich in electron density.

IR Spectral Studies: IR spectra of ligand and its metal complexes were recorded on Perkin-Elmer infra spectrophotometer model 577. The changes in the characteristic group frequencies of ligand on chelation with metal ions can be presumed to be on account of the coordination.

The presence of a weak band in the spectra of the ligand in the vicinity of 2680–2500 cm^{-1} points to hydrogen bonding and further indicates the presence of hydrogen bonded —OH stretching of carboxylic groups.[11-13] Hydrogen bonding as is well established lowers the frequency of the bonded groups, so the band expected somewhere near 3300 cm^{-1} on account of carboxylic acid —OH is found to be missing from the spectrum of the ligand and is explained due to very strong hydrogen bonding.

The vibrations at 3065 and 3045 cm^{-1} are attributed to ν_{asym}(NH)[14–16] in the chelating agent whereas the symmetric NH vibration occurs overlapped with ν(CH) at 3010 cm^{-1}. The absence of these bands from the spectra of the complexes suggests that the metals are chelated at NH site.[17, 18] The 3045 and 3065 cm^{-1} absorptions are converted with a slight shift into a shoulder on OH stretching band at 3500–3100 cm^{-1} on account of the presence of water molecules in most compounds and this shoulder may be taken to be, although not very convincingly, as a negative shift of ν(NH). The vibrational frequency part of ν(CH) is sometimes observed at 3010 and is recognised on account of its reduced intensity. The weakening of the —NH stretching and splitting of the band to higher frequency is caused by the drainage of the electrons from the nitrogen to the metal atom.[19, 20]

The CN stretching vibrations overlap with CH_2 bending or wagging modes and occur in the region[16] 1520–1090 cm^{-1}. The bands in the ligand occur[21–23] at 1550, 1460 and 1340 cm^{-1}. The other vibrations at 1285, 1055 and 1275, 1100 cm^{-1} are the mixed ν(CN) + δ(NH) vibrations.

As the coordination of metal ions on NH site is known to cause a positive shift to ν(CN) stretchings, at the frequencies mentioned for ν(CN) + δ(NH) are observed to be shifted to higher values and many a time splitted with ν(CN) part as a separate weak band. The band at *ca.* 1550 cm^{-1} was erroneously assigned to NH in-plane bending by previous workers[24] as the normal coordinate treatment has shown it to be due to CH bonding coupled with CN vibrations.

The NH in-plane bendings at 1280 cm^{-1} and 1100–1055 cm^{-1} suggest more pronounced effect in the spectra of metal complexes and are explained to be on account of the nature of mixed vibrations. In most of these cases the bands record a positive shift and thus support the contention of the metals being coordinated with NH. The NH rocking vibration assigned to 770–750 cm^{-1} also follows the above trend of shift to higher wave numbers and confirms the metals' linkage with NH group.[24, 25]

A more convincing proof of metals coordinated at NH site is derived from the appreciable changes in the absorption frequency ν(C—N—C) in the spectra of thiazolidone.[26] This band for ν(C—N—C) is attributed at and around 1170–1145 cm^{-1} is completely vanished from the spectra of compounds and confirms metal to NH bonding.

The endo-cyclic C—S stretching bands near 860, 705 and 625 cm^{-1} for the ligand thiazolidine-4-carboxylic acid are comparable with those of simple and n-alkyl dithiocarbamates[27], which have asymmetric and symmetric C—S frequencies near 820 and 620 cm^{-1}. Geetharani *et al.*[20] on normal coordinate analysis of thiazolidine-2-thione, have also evaluated the C—S frequencies to occur at 655 and 620 cm^{-1} besides a band at 1060 cm^{-1} which is registered in the present case at 1055 cm^{-1}. The C—S vibrations are shifted to higher values in almost all the complexes on account of an increased d_π–p_π contribution of sulphur in a ring

π-system.[28] Iron and copper complexes, however do not observe this pattern; instead, a definite red shift for all these vibrations attributed to ν(CS) is registered. Thus it is inferred that the iron and copper possibly are attached at sulphur site which is sterically only possible when there is stacking of molecules one over the other.

The positive shift of the bands in the spectra of the chelates except that of copper suggests that sulphur is not a coordination site.[29] The negative shift of the ν(C—S) frequencies in IR spectrum of copper, however, suggests that the metal is bonded through sulphur.

The composite frequencies recorded at 1380–1375 cm^{-1} and 1315–1310 cm^{-1} attributed to ν(CS) mode with small contribution of ν(CN)[30–31] shift to higher wave numbers in complexes. Splitting of these bands and their inconsistent behaviour in different complexes is not helpful in providing any clue to the mode of metal bondage with the ligand.

A broad band in 1740–1700 cm^{-1} region and an absorption at 1635–1625 cm^{-1} in the spectra of the ligand suggest the presence of carboxylate group both in dissociated and undissociated forms.[32] These vibrations are attributed on account of asymmetric stretch of the carboxylate anion. The symmetric stretch of COO is registered at around 1460—1455 cm^{-1} and thus indicates a difference of $\Delta\nu$(COO) of 170–175 cm^{-1}.

The effect and type of coordination are usually judged from the magnitude of separation of ν_{asym}(COO) and ν_{sym}(COO) frequency shifts[32, 33] *i.e.* a free ion carboxylate group[34] usually has a $\Delta\nu(COO^-)$ of 200 cm^{-1}. A monodentate carboxylic group has a difference of 150–100 cm^{-1}, but a bidentate or bridging carboxylate has a much narrow difference (< 120 cm^{-1})[34–35]. In the unidentate complexes ν(C$\overset{\cdot\cdot}{=}$O) is higher than $\nu_{asym}(COO)^-$ and $\nu(COO)^-$ is lower than $\nu_{sym}(COO)^-$ and a larger separation results between two ν(COO) than in the free ion of COO^-. The opposite trend is observed in the bidentate chelation of the carboxylic group and it makes the separation narrower between the two $\nu(COO^-)$ than that in the free ligand. However, it was observed that frequencies responsible for $\nu(COO^-)$ exhibit almost the same values of separation as that of the free ion in the bridged complexes. Therefore, the degree of separation of frequencies as a criteria for deterrmining bidentate or bridged structure cannot always be a true guide or relied upon. Another better way is to look for direction of change. A bidentate or bridged behaviour of COO group is inferred if the stretching vibrations ν(COO) change in the same direction on complexation.[36]

The spectra of complexes of Co^{2+}, Ni^{2+}, Zn^{2+} and Hg^{2+} of the ligand show an increase in antisymmetric frequencies ν_{asym}(COO) and a decrease in $\nu_{sym}(COO^-)$, hence suggest beyond doubt that metals form carboxylates through deprotonation. The separation value $\Delta\nu_{asym}$(COO) and $\nu_{sym}(COO^-)$ are always larger than that of ligand.

Since an increase of the covalent character of the metal-oxygen bond leads to more symmetrical carboxyl group and consequently results in an increase in the frequency separation of the COO^- stretchings, the order of separation is evaluated as the order of covalent character of M—O bond. The stretching vibrations COO^- as are shifted to lower values in thiazolidinones Fe, Cu, Zn and

Hg may apparently mislead to conclude bridge nature of carboxy moiety. However, with nitrogen which is also taking part in the coordination apparently forming five membered chelate ring, the bridge nature of carboxy moiety is not possible. It is, therefore, safer to depend only on $\Delta\nu$(COO) and presume COO^- nature to be monodentate even in these compounds as well.

The in-plane bending frequency *ca.* 1435–1430 cm^{-1}, a characteristic group frequency for hydroxy part of carboxylate ion in the spectra of the ligand, is either shifted to lower vibrations or is completely washed off from the spectra of metal complexes. It is thus affirmative that metals are coordinated through deprotonation. The deprotonation of COOH on complexation is also confirmed as the out--of-plane frequency attributable to 950–945 cm^{-1} registers a parallel behaviour to that of the in-plane OH vibrations.

REFERENCES

1. G. Pneumatikakis and N. Hadziliatis, *J. Inorg. Nucl. Chem.*;**15**, 429 (1979).
2. H.V. Aposhiam, *Science*, **93**, 128 (1958).
3. J.H. Walshe, *Am. J. Med.*, **21**, 487 (1956).
4. H.V. Aposhiam and M.M. Aposhiam, *J. Pharm. Co. Exp. Ther.*, **126**, 131 (1959).
5. J. Dehand, J. Jordanov, F. Keck, A. Mossett, D.J. Bennet and J. Gatty, *Inorg. Chem.*, **18**, 1543 (1979).
6. D.P. Graddon, *Coord. Chem. Rev.*, **4**, 327(1969).
7. S. Ratner and H.T. Clarke, *J. Am. Chem. Soc.*, **59**, 200 (1937).
8. P. Singh, V. Singh, G.P. Pokhariyal, R. Pal and R.P. Mahesh, *J. Indian Chem. Soc.*, **57**, 259 (1980).
9. A. Earnshaw, Introduction to Magneto-Chemistry, Academic Press, London (1968).
10. R.W. Jotham and S.F.A. Kettle, *J. Chem. Soc. (A)*, 2816, 2821 (1969).
11. S. Yoshida and M. Asai, *Pharm.* Bull., **7**, 162 (1959).
12. D. Sutton, Electronic Spectra of Transition Metal Complexes, McGraw-Hill, London (1968).
13. T.R. Harkins, J.L. Walter, O.E. Harris and F. Freiser, *J. Am. Chem. Soc.*, **78**, 260 (1956).
14. P.K. Gosavi, U. Agrawal and C.N.R. Rao, *J. Am. Chem. Soc.*, **89**, 2235 (1967).
15. A. Kowai and B.B. Kedzia, *Acad. Polon. Sci. Ser. Sci. Chem.*, **24**, 559 (1976).
16. A.S. Mahajan, Ph.D. Thesis, Nagpur University, Nagpur (1978).
17. K. Nakanishi, Infrared Absorption Spectroscopy, Narkodo Co. Ltd., Tokyo, p.16 (1964).
18. U. Agarwala and L. Agarwala, *J. Inorg. Nucl. Chem.*, **34**, 255 (1972).
19. D. Fak-Michalaka and B.B. Kedzia, *Acad. Polan. Sci. Soc. Sci. Chim.*, **24**, 393 (1976).
20. K. Geetharani and D.N. Sathyanarayana, *Indian J. Chem.*, **14A**, 170 (1976).
21. Narayan S. Bhave and K.B. Kharat, *J. Indian Chem. Soc.*, **57**, 871 (1987).
22. K.P. Srivastava and N.K. Agarwal, *Z. Anorg. Allg. Chem.*, **393**, 168 (1977).
23. Y. Yamaguchi, R.B. Ponland, S. Mizushima, T.J. Lane, C. Curran and J.B. Quagland, *J. Am. Chem. Soc.*, **80**, 527 (1958).
24. C.F. Sratos, S. Mizushima, C. Curran and J.V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957).
25. S. Mizushima, I. Nakagawa and J.V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).
26. D. Venkappayya and D.H. Brown, *J. Inorg. Nucl. Chem.*, **36**,.1023 (1974).
27. K. Makamotary, T. Gujalo, R.A. Condrate and Y. Morimate, *J. Chem. Phys.*, **39**, 423 (1963).
28. D.F. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel and L.E. Sutton, *J. Chem. Soc.*, 332 (1954).

29. C. Fregni, C. Prefi and G. Tosi, *J. Inorg. Nucl.Chem.*, **36**, 3695 (1974).
30. R.K. Gosavi and C.N.R. Rao, *J. Inorg. Nucl. Chem.*, **29**, 1037 (1967).
31. R.K. Gosavi, U. Agarwala and C.N.R. Rao, *J. Am. Chem. Soc.*, **69**, 235 (1967).
32. K. Nakamoto, Y. Norimoto and A.E. Markell, *J. Am. Chem. Soc.*, **83**, 4528 (1961).
33. K. Nakamoto, J. Fujika, S. Tanaka and M. Kabayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).
34. N.F. Curtis, *J. Chem. Soc. (A)*, 1579 (1968).
35. K. Dey and K.C. Ray, *J. Indian. Chem. Soc.*, **50**, 66 (1973).
36. K. Nakamura, *J. Chem. Soc. (Japan)*, 79, 1411 (1958).

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