

Synthesis and characterization of Cu(I) and Ag(I) complexes of 4,5-diphenylimidazole-2-thione

A MOHANAN and K K ARAVINDAKSHAN*

Department of Chemistry, University of Calicut, Calicut 673 635, India

MS received 26 September 1988; revised 5 December 1988

Abstract. A series of complexes of Cu(I) and Ag(I) with 4,5-diphenylimidazole-2-thione (L2H) have been isolated and characterized by chemical analyses, electrical conductance, magnetic and IR spectral data. These studies revealed that the ligand coordinates with the central metal ion in one of the following ways: (1) neutral monodentate, (2) anionic bidentate or (3) S-coordinate with an additional M–N interaction.

Keywords. 4,5-Diphenylimidazole-2-thione; electrical conductance; magnetic data; spectral data.

1. Introduction

Imidazole-2-thiones have found applications in clinical medicine because of their pharmacological activities (Hofmann 1953). A number of them have antithyroid activities which are many times higher than the activity of thiouracil (Stanley and Astwood 1947). Most of the work done on the donor properties of this type of ligand is concerned with imidazolidine-2-thione, its derivatives, imidazole-2-thione and its N-mono- or N,N'-dialkyl substituted compounds. It has been shown that this type of heterocyclic thione is capable of reducing metals in higher oxidation states and stabilizing their complexes in lower oxidation states (Morgan and Burstal 1928; Devillanova and Verani 1977). A search through the literature showed that no systematic studies on the transition metal complexes of aryl substituted imidazole-2-thiones, in general, and of 4,5-diphenylimidazole-2-thione, in particular, have been carried out so far. This type of ligand not only provides a variety of potential donor sites such as –NH and C=S, but also induces steric hindrance by virtue of the presence of bulky substituents at the 4- and 5-positions of the imidazole ring. It is therefore considered worthwhile to study copper and silver complexes of 4,5-diphenylimidazole-2-thione, L2H[†] (chart 1) from the point of view of electrical conductance, magnetic and spectral behaviour.

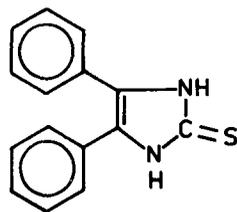


Chart 1

* For correspondence

† Chem. Abstr. name: 4,5-Diphenyl-1,3-dihydro-2H-imidazole-2-thione

2. Experimental

2.1 Materials

All chemicals used were BDH 'AnalaR' quality. Commercial solvents used for syntheses were purified by standard methods. The solvents used for spectral and conductivity measurements were BDH spectroscopic grade reagents.

2.2 Synthesis of ligand

4,5-Diphenylimidazole-2-thione was synthesised according to a reported method (Purushothaman 1985) by refluxing a mixture of benzoin (10.0 g, 0.05 mol) and ammonium thiocyanate (9.4 g, 0.12 mol) in isoamyl alcohol (250 ml) for about 1 h. The crystalline material that formed was filtered, washed with water and then with ether and dried. It was recrystallised from methanol (m.p. 325°C).

2.3 Synthesis of complexes

Complexes of L2H were readily synthesised by reacting the ligand in methanol with the approximate copper or silver salt in methanol or water. The metal salt to ligand ratio was maintained as 1:1 during the synthesis. All the Cu(I) complexes, except Cu(LH), where LH is the monoanion of L2H, were prepared by reducing the respective Cu(II) salt with the ligand. Cu(LH) was prepared by refluxing cuprous chloride dissolved in aqueous ammonia with a methanolic solution of the ligand. Ag(LH) was prepared using a hot aqueous solution of silver acetate. In all cases (except in the case of the silver nitrate complex) complexes separated on refluxing the reaction mixture for 15 min to 1 h. However, in the case of the silver nitrate complex, the synthesis was carried out at room temperature. The solid complex that separated in each case was filtered, washed with methanol or water and dried *in vacuo* over P_4O_{10} .

2.4 Analyses

The complexes were analysed by standard methods (Vogel 1978) to determine the percentage of metal, sulphur and halogen (if any) present in them. Nitrogen was determined microanalytically.

2.5 Physical measurements

The molar conductance measurements of the complexes were carried out using their 10^{-3} M DMF and nitrobenzene solutions on a Biochem conductivity bridge type M-70 at $28 \pm 2^\circ\text{C}$. The magnetic susceptibilities were determined at room temperature by the Gouy method. The reflectance spectra were obtained on a Shimadzu spectrophotometer SP 200. Infrared spectra of the ligand and the complexes, in the range $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Perkin Elmer 397 spectrophotometer, using the KBr disc technique.

3. Results and discussion

3.1 Formulation and general properties of the complexes

The chemical analyses (table 1) confirm the following stoichiometries for the complexes: $M(L_2H)X$, when $M = Cu(I)$, $X = Cl, Br, NO_3$ or $0.5SO_4$, and when $M = Ag(I)$, $X = NO_3$ or $0.5SO_4$; and $M(LH)$, where $M = Cu(I)$ or $Ag(I)$. All these complexes are air- and photo-stable and are nonhygroscopic in nature. They are soluble in DMF, but sparingly soluble in other organic solvents.

3.2 Electrical conductance

A comparison of the observed molar conductance values in DMF (table 1) with the reported data (Geary 1971) shows that the complexes, $Cu(LH)$ and $Ag(LH)$ are nonelectrolytes. According to the molar conductance values $Cu(L_2H)Cl$, $Cu(L_2H)Br$, $Cu(L_2H)NO_3$ and $Ag(L_2H)NO_3$ undergo complete dissociation and behave as 1:1 electrolytes in DMF. However, in nitrobenzene the molar conductance values of $Cu(L_2H)Cl$ and $Cu(L_2H)Br$ show that they are nonelectrolytes. The sulphate complexes, $Cu(L_2H)0.5SO_4$ and $Ag(L_2H)0.5SO_4$ show a certain degree of dissociation in DMF as their molar conductance values are much lower than the expected value for a 1:1 electrolyte.

Table 1. Analytical and molar conductance data for $Cu(I)$ and $Ag(I)$ complexes.

Complexes	Found (Calcd) (%)				Molar conductance ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ at 10^{-3}M) in	
	Metal	N	S	Halogen	DMF	Nitrobenzene
$[Cu(L_2H)Cl]$	18.05 (18.09)	7.97 (7.99)	9.12 (9.13)	9.98 (10.09)	75.9	2.0
$[Cu(L_2H)Br]$	16.01 (16.05)	7.07 (7.05)	8.00 (8.10)	20.08 (20.19)	79.4	1.5
$[Cu(L_2H)]NO_3$	16.69 (16.82)	7.41 (7.60)	8.42 (8.48)	—	61.4	Sparingly soluble
$[Cu(L_2H)0.5SO_4]$	17.43 (17.46)	7.69 (7.75)	13.10 (13.22)	—	12.8	Sparingly soluble
$[Cu(LH)]$	20.10 (20.18)	8.89 (8.92)	10.10 (10.18)	—	1.7	Sparingly soluble
$[Ag(L_2H)]NO_3$	25.54 (25.55)	6.63 (6.66)	7.48 (7.59)	—	93.3	Sparingly soluble
$[Ag(L_2H)0.5SO_4]$	26.42 (26.42)	6.86 (6.90)	11.62 (11.78)	—	20.5	Sparingly soluble
$[Ag(LH)]$	30.01 (30.03)	7.79 (7.83)	8.83 (8.93)	—	0.3	Sparingly soluble

3.3 Magnetic properties and electronic spectra

The magnetic measurements show that all the complexes under investigation are diamagnetic as expected for a d^{10} electronic configuration. The very rapid reduction of Cu(II) demonstrates the much stronger interaction of a soft donor, such as sulphur with the soft metal ion Cu^+ , than with the hard Cu^{+2} ion. The above observations are supplemented by the electronic spectral studies of the complexes, which do not display any characteristic absorption bands in the visible region.

3.4 Infrared spectra

The broad band of very strong intensity at about 3000 cm^{-1} in the ligand spectrum may be assigned to $\nu(\text{N-H})$. The broad nature of this band and its position at a lower frequency region are indications of the presence of $\text{NH} \dots \text{S}$ hydrogen bonding in the solid ligand (Form *et al* 1976). In the complexes these bands are shifted to higher wavenumbers indicating coordination of the ligand through sulphur atom. In the solid state there is no S-H group in the free ligand, which is confirmed by the absence of any band in the regions $2650\text{--}2500\text{ cm}^{-1}$ in its spectrum (Bellamy 1978).

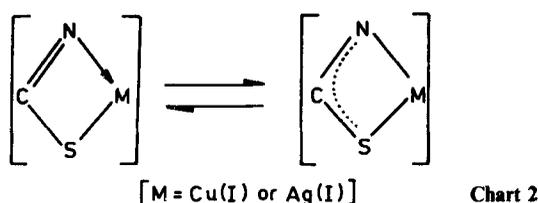
All organic compounds containing the thioamide group, H-N-C=S give rise to four thioamide bands (Rao and Venkataraghavan 1962). Bands of very strong intensity at 1500 and 1480 cm^{-1} (with shoulders at 1510 and 1450 cm^{-1}) are the I thioamide bands. They are due to the coupled bands arising from $\nu(\text{C-N})$ and $\delta(\text{C-H})$ which has been split because of the presence of two thioamide groups in the ligand. According to the changes in the nature of this band during complexation, the complexes under investigation can be grouped into three. In the complexes Cu(L2H)Cl , Cu(L2H)Br , Ag(L2H)NO_3 and $\text{Ag(L2H)O}\cdot 5\text{SO}_4$, this band is found as a singlet at 1518 cm^{-1} . The shift of this band to the higher frequency region and its singlet nature indicate the absence of N-coordination in these complexes. In Cu(LH) and Ag(LH) this band is split and exhibits a shift to lower wavenumbers and is found in the region 1485 and 1460 cm^{-1} . These are clear indications of the participation of a nitrogen atom, in addition to the sulphur atom, in the coordination in these two complexes (Raper and Crackett 1981). However, in the nitrate and sulphate complexes of copper, the behaviour of this band is quite complex. Here the shift for this band to the lower frequency region is less when compared to that of the complexes mentioned above with N-coordination, but it is found to be split. This shows that there may be some sort of interaction between the metal ion and one of the nitrogen atoms of the ligand, which can be treated as a very weak bond. A band of medium intensity at 810 cm^{-1} can be assigned to the thioamide band IV. It has contributions from $\nu_s(\text{C=S})$, $\nu_{as}(\text{C=S})$, ring deformation, $\nu(\text{C-N})$ etc. However, in the spectra of all the complexes, this band disappears and a new band of weak intensity appears around 630 cm^{-1} . Such a large shift for band IV on S-coordination of similar ligands has been reported (Singh and Singh 1984). The pure $\nu(\text{C=S})$ band at 558 cm^{-1} in the ligand spectrum is displaced to the lower wavenumber region by about $10\text{--}20\text{ cm}^{-1}$, which is consistent with the observed changes for band IV on coordination through the sulphur atom. The weak band around 490 cm^{-1} in the spectra of Cu(LH) and Ag(LH) may be attributed to $\nu(\text{M-N})$.

The presence of ionic nitrate is indicated by the new bands at about $1360\text{--}1320\text{ cm}^{-1}$ (ν_1) and at 830 cm^{-1} (ν_2) in the spectra of nitrate complexes (Curtis and Curtis 1965). For a bidentate sulphate radical the expected bands are ν_1 and ν_2 at 990 and 460 cm^{-1} ,

and ν_3 and ν_4 each split into bands around 1160, 1120 and 1080 cm^{-1} and 625, 610 and 595 cm^{-1} respectively (Nakamoto 1970). In the case of $\text{Cu}(\text{L2H})\cdot 5\text{SO}_4$ all these bands are seen in the expected region, whereas for $\text{Ag}(\text{L2H})\cdot 5\text{SO}_4$ ν_3 is broad though its splitting is not clear, and at the same time ν_4 is split.

4. Conclusion

Thus on the basis of the foregoing discussion it is inferred that the ligand (L2H) acts as a neutral monodentate one coordinating through the thione sulphur atom in all the complexes, except in those of the general formula $\text{M}(\text{LH})$. In the nitrate and sulphate complexes of copper an additional M–N interaction is expected. In the complexes of general formula $\text{M}(\text{LH})$, the ligand acts as an anionic bidentate, coordinating through the sulphur atom and one of the ring nitrogens (chart 2).



Complexes of imidazole–thione of this type are rare. However, it is not unlikely as the ligand, (L2H) can exist in thioenol form in solutions of $\text{pH} \leq 7$ (Butler *et al* 1983) and hence chelate after deprotonation as a thiolate anion, (LH).

Acknowledgements

The authors thank Professor K T Rama Varma, for encouragement. The award of a fellowship by the University Grants Commission to one of the authors (AM) is gratefully acknowledged.

References

- Bellamy L J 1978 *The infrared spectra of complex molecules* (London: Chapman and Hall)
 Butler L M, Creighton J R, Oughtred R E and Raper E S 1983 *Inorg. Chim. Acta* **75** 149
 Curtis N F and Curtis Y M 1965 *Inorg. Chem.* **4** 804
 Devillanova F A and Verani G 1977 *Transition Metal Chem.* **2** 120
 Form G R, Raper E S and Downil T C 1976 *Acta Cryst.* **B32** 345
 Geary W J 1971 *Coord. Chem. Rev.* **7** 81
 Hofmann K 1953 *The chemistry of heterocyclic compounds* (New York: Interscience)
 Morgan G T and Burstal F H 1928 *J. Chem. Soc.* 143
 Nakamoto K 1970 *Infrared spectra of inorganic and coordination compounds* (New York: John Wiley)
 Purushothaman E 1985 *Studies in the photochemistry of imidazole derivatives*, Ph.D. thesis, University of Calicut, Calicut
 Rao C N R and Venkataraghavan P 1962 *Spectrochim. Acta* **18** 541
 Raper E S and Crackett P H 1981 *Inorg. Chim. Acta* **50** 159
 Singh J and Singh N K 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 125
 Stanley M M and Astwood E B 1947 *Endocrinology* **41** 66
 Vogel A I 1978 *A text book of quantitative inorganic analysis* (London: ELBS-Longman)