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Isoperthiocyanic Acid (3-amino-5-thione-1,2,4-dithiazole): an Exocyclic Sulphur Donor Ligand

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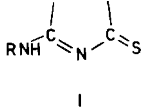
The first metal complexes employing isoperthiocyanic acid (L) as a ligand, namely $MCl_2(L)_2$ (M = Pd(II) and Pt(II)) and $CuCl(L)_2$, have been prepared and characterized. Infrared spectroscopic results suggest that the palladium and platinum complexes possess a cis-*square planar geometry whereas the copper(I) complex is a chlorine-bridged tetrahedral species. X-ray photoelectron spectroscopic results indicate that isoperthiocyanic acid acts as a monodentate ligand in these complexes utilizing the exocyclic thione sulphur atom. Similarities between the S 2p binding energy spectra of this ligand and 1,2-dithiole-3-thione derivatives are noted.*

Introduction

Isoperthiocyanic acid, or 3-amino-5-thione-1,2,4-dithiazole (I; R = H) was first isolated [1] by Wöhler in 1821, but its structure was not resolved for 140 years. In 1961 Hordvic [2] published electron-density maps which showed the presence of two adjacent sulphur atoms in a five-membered ring and he also considered that his work gave some indication that both hydrogen atoms might be present as an exocyclic amino-group. Subsequent infrared evidence [3] was consistent with structure (I; R = H) for the acid.



I

The acid character of (I; R = H) has been shown [4] in ring-opening reactions with bases such as ammonia, amines and hydroxide ion. Recently the basicity of (I; R = H) has been illustrated [5] by protonation of the exocyclic amino-group and by reactions with acetic anhydride and phenyl isocyanide to produce (I; R = COMe and CONHPh) respectively. The acid has also been suggested [6] as an analytical reagent for the selective detection of nitrite ion.

We report here the first use of the acid as a ligand in metal complexes. Our interest in this compound rests with the number of potential sites available for coordination to metal ions. In principle, the ligand may bind through the exocyclic thione sulphur or amino nitrogen atoms thereby showing a relationship to ligands such as thiourea, thiosemicarbazide or thiocarbohydrazide, or through the endocyclic nitrogen or sulphur atoms, a comparison with the ligand behavior of thiazoles then being appropriate.

Experimental

Infrared spectra (4000–250 cm^{-1}) of nujol and hexachlorobutadiene mulls were obtained using a Perkin–Elmer 621 spectrophotometer. Low frequency infrared spectra (400–40 cm^{-1}) were obtained from samples dispersed in polyethylene using a Beckman-R.I.I.C. FS 720 interferometer. Mass spectra were obtained using an A.E.I. MS 12 instrument and ^1H n.m.r. spectra in $(CD_3)_2SO$ on a Varian A60 spectrometer. Magnetic susceptibility measurements were made by the Gouy method.

X-ray photoelectron spectra were recorded using a Hewlett–Packard 5950A ESCA spectrometer. The aluminium $K\alpha_{1,2}$ line (1486.6 eV) was used as the excitation source. Sample preparation and full details of the experimental procedure are described fully elsewhere [7, 8].

Isoperthiocyanic acid was prepared by collecting the yellow crystalline deposit formed by allowing a dilute aqueous solution of thiocyanic acid to stand at ambient temperatures for a few days. The thiocyanic acid solution was obtained by vacuum distillation at room temperature of a solution of potassium thiocyanate (50 g) in water (100 cm^3) and 5 M sulphuric acid (90 cm^3). The distillate (75 cm^3) was collected in an ice-cooled receiver. Alternatively the method of Klason [9] was employed. *Anal.* Found: C, 16.3; H, 1.38; N, 19.0. $C_2H_2N_2S_3$ requires: C, 16.0; H, 1.34; N, 18.7%.

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TABLE I. Significant Infrared Bands (cm^{-1}).

Assignment	L^a	d^2-L^b	CuCl(L)$_2$	PdCl$_2$(L)$_2$	PtCl$_2$(L)$_2$
ν(NH$_2$)$_{as}$	3220 m	2390 m 2340 sh	3245 m	3240 m	3270 m
ν(NH$_2$)$_s$	3020 m 2945 sh	2210 ms	3080 m	3080 m 2920 m	3110 m 2950 mw
δ(NH$_2$)	1626 s	1246 m	1618 s	1614 s	1611 s
ν(C=N)	1514 s	1535 s	1511 s	1504 s	1510 s
ν(C=N) coupled	1305 s	1325 s 1300 sh	1321 s	1330 m	1311 m
NH$_2$ rock	1082 m	792 w	1077 mw	1068 w	1080 m
ν(C=S) coupled	1000 s	1007 s	1012 m	997 m	1002 m
NH$_2$ wag	625 s	–	631 m	629 s	633 m
ν(MCl)	–	–	200 m 188 m	349 s 342 s	330 s 323 s

[a] L = Isoperthiocyanic acid. [b] d^2-L = Perdeuteroisoperthiocyanic acid.

Perdeuteroisoperthiocyanic acid was prepared as follows. (I; R = H), (0.28 g) was dissolved in anhydrous tetrahydrofuran (35 cm^3) under nitrogen, and deuterium oxide (> 99.7% purity; 2.9 g) added. The solution was stirred for 20 min. and then taken to dryness *in vacuo*. The solid was then retreated with deuterium oxide (2.1 g) in tetrahydrofuran (35 cm^3) for 1 h before isolation as above.

Dichlorobis(3-amino-5-thione-1,2,4-dithiazole)-platinum(II)

Platinum(II) chloride (0.15 g) and (I; R = H) (0.17 g) were stirred in anhydrous acetonitrile or diglyme (50 cm^3) at ambient temperatures under nitrogen for 4 h. The resulting yellow solid was filtered off, washed with warm acetonitrile or diglyme to remove excess ligand and dried *in vacuo*. *Anal.* Found: C, 8.55; H, 1.06; N, 10.0. $C_4H_4Cl_2N_4PtS_6$ requires: C, 8.48; H, 0.72; N, 9.90%.

Dichlorobis(3-amino-5-thione-1,2,4-dithiazole)-palladium(II)

Palladium(II) chloride (0.24 g) and (I; R = H) (0.40 g) were either stirred at ambient temperatures in anhydrous acetonitrile or diglyme (60 cm^3) or heated together in either of these solvents under gentle reflux. The red-brown solids were filtered off, washed with warm acetonitrile or diglyme and dried *in vacuo*. The products had identical infrared spectra and analyses which were in close agreement. *Anal.* Found: C, 10.2; H, 1.22; N, 11.5. $C_4H_4Cl_2N_4PdS_6$ requires: C, 10.1; H, 0.84; N 11.7%.

Chlorobis(3-amino-5-thione-1,2,4-dithiazole)copper (I)

(a) Anhydrous copper(II) chloride (0.32 g) and (I; R = H) (0.70 g) were heated in refluxing anhydrous acetonitrile (30 cm^3) for 18 h under nitrogen. The light brown solid product was filtered off, washed well with acetonitrile and dried *in vacuo*.

(b) Copper(I) chloride (0.16 g) and (I; R = H) (0.50 g) were stirred in anhydrous diglyme or tetrahydrofuran (30 cm^3) for 4 h at ambient temperatures. The product was filtered off, washed with diglyme or tetrahydrofuran and dried *in vacuo*. The products from routes (a) and (b) had identical infrared spectra and closely similar analyses. *Anal.* Found: C, 12.8; H, 0.91; Cl, 8.80; Cu, 15.4; N, 14.9. $C_4H_4ClCuN_4S_6$ requires: C, 12.0; H, 1.01; Cl, 8.87; Cu, 15.9; N, 14.0%.

Results and Discussion

Isoperthiocyanic acid has been shown [2, 3] to have structure (I; R = H). We have prepared this acid by two routes and to confirm both the purity and identical nature of the products, the infrared, n.m.r. and mass spectra of samples were recorded. The infrared spectra (Table I) were in acceptable agreement with that previously reported [3] between 4000 and 400 cm^{-1}, further bands being found at 263(m), 254(m), 191(m), 147(m) and 125(s) cm^{-1} in the previously unexplored low-frequency region. N.m.r. and mass spectral data have not been reported before. The ^{1}H n.m.r. spectrum in $(CD_3)_2SO$ shows only a broad singlet at 0.35 τ due to the exocyclic amino protons, the broadening of the signal being due to the influence of the neighboring ^{14}N nucleus. The mass spectrum (70 e.v. ionizing energy; source temperature 100 °C) shows the fragments listed in Table II, m/e values being based on the most abundant atomic isotopes. Each fragment ion appears in the spectrum as a cluster of peaks due to the detection of species involving ^{13}C, ^{15}N, ^{33}S and ^{34}S isotopes. Low

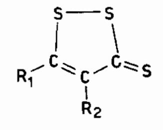
TABLE II. Mass Spectrum of Isoperthiocyanic Acid.

m/e	Ion	Relative Intensity
150	P^+	6
118	$(P - S)^+$	17
84	$C_2N_2S^+$	15
76	CS_2^+	4.4
60	$SCNH_2^+$	36
59	$HSCN^+$	100
58	SCN^+	14
44	CS^+	16
34	H_2S^+	10
32	S^+	54
28	N_2^+	40
27	HCN^+	24

intensity 'M + 2' ions associated with the presence of ^{34}S (4.2% natural abundance) were particularly evident. Ion abundances quoted in the Table have been obtained by summation of the isotope contributions observed for each ion.

Confirmation of the above spectral features and of the original infrared assignments [3] was provided by the preparation and examination of perdeutero-isoperthiocyanic acid. This product gave, as anticipated, a featureless ^1H n.m.r. spectrum and a parent ion at m/e 152 in the mass spectrum. As shown in Table I, the only infrared bands of the acid to show significant shifts on deuteration are those assigned to modes associated primarily with the exocyclic amino-group. This result provides additional confidence in the original assignments.

The X-ray photoelectron spectrum of this acid exhibits the set of core electron binding energies presented in Table III. The existence of two C 1s binding energies is in accord with the presence of two distinct carbon environments and therefore resembles the related C 1s spectra of other 5-membered ring systems (*e.g.,* thiazole) [10]. The endocyclic and exocyclic nitrogen atoms have similar N 1s binding energies (~ 399.6 eV) which were not resolvable within the present limits of instrumental resolution. However, the spectral feature which is most characteristic of this ligand is the S 2p binding energy spectrum (Table III and Fig. 1). The presence of two S 2p binding energies at 164.4 and 162.3 eV (in the intensity ratio of 2:1) is reminiscent of the related spectra of 1,2-dithiole-3-thione derivatives of the type (II) [11]. For these latter systems, the corresponding S 2p energies are ~ 164.4 and 162.2 eV, almost identical with those we have found for isoperthiocyanic acid.



II

The basicity of isoperthiocyanic acid has previously been demonstrated [5] by protonation of the amino-group using hydrogen chloride in acetonitrile. However we believed that in reaction with suitable metal compounds the acid (L) may be capable of acting as a ligand by donation of electron density not only from the amino-nitrogen atom, but also from the exocyclic thione sulphur atom, or even from the endocyclic donor atoms. We have been able to prepare three complexes, $PdCl_2(L)_2$, $PtCl_2(L)_2$, and $CuCl(L)_2$ which illustrate for the first time the ability of L to act as a ligand. Since the ligand was found to be essentially insoluble in water, dichloromethane, chloroform and ether, only slightly soluble in acetone, methanol and ethanol, but more soluble in dimethylsulphoxide, diglyme, tetrahydrofuran and acetonitrile, the latter solvents were employed in the preparations. Unfortunately the three complexes isolated were too insoluble and involatile for molecular weight, n.m.r. and mass spectral measurements. Our measurements were restricted to infrared and X-ray photoelectron spectroscopy and magnetic susceptibility measurements. The three complexes were found to be diamagnetic at room temperature confirming the metal oxidation states suggested. The copper complex, $CuCl(L)_2$, has been prepared from both copper(I) and copper(II) chlorides showing that this ligand, like several other sulphur donor ligands such as thiourea and other thiones [12], is capable of reducing copper(II) to copper(I).

Bands of strong to medium intensity (Table I) absent from the free ligand spectrum, have been found in the low-frequency infrared spectra of the complexes. These are assigned to ν(MCl) stretching modes by comparison with many other similar studies [13]. The detection of two ν(PdCl) and ν(PtCl) bands suggest that these complexes possess *cis*-planar geometries (C_{2v}; ν(MCl) $A_1 + B_1$). In view of the rather bulky nature of (I; R = H) it is perhaps surprising to find the *cis*-configuration preferred, although such an arrangement allows the greatest amount of back donation from metal d_π-orbitals if the ligand is sulphur-bonded, thus enhancing the M–L bond strength. Two bands assignable to ν(CuCl) are also found, but at much lower frequencies, for the copper(I) complex. The low frequencies of the bands tend to rule out the presence of terminal Cu–Cl bonds such as would occur in a monomeric trigonal planar structure (*cf.* ν(CuCl) of 255 cm^{-1} for trigonal planar $CuCl[P(C_6H_{11})_3]_2$ [14]). The data are however consistent with copper–chlorine bridge bonds which would be present in a dimeric structure with a tetrahedral array of ligands around the copper atoms (*cf.* ν(CuCl) of 232 and 162 cm^{-1} for $[CuCl(o\text{-}NMe_2C_6H_4AsMe_2)]_2$ [15]).

TABLE III. X-ray Photoelectron Spectra of Isoperthiocyanic Acid and its Complexes^{a}.

Binding Energies (eV)	Isoperthiocyanic Acid (L)^{b}	$CuCl(L)_2$	$PtCl_2(L)_2$
C 1s	287.3(2.2); 284.8(2.2)	288.0; 285.0	287.3; 284.9
S 2p (–*S*–*S*–)^{c}	164.3(1.8)	164.3	164.5
S 2p (C=*S*)^{c}	162.3(1.8)	162.9	163.2
N 1s	399.6(2.0)	400.0	399.7
Cl 2p$_{3/2}$	–	198.2	198.0
Cu 2p$_{1/2}$ or Pt 4f$_{5/2}$	–	953.1	76.0
Cu 2p$_{3/2}$ or Pt 4f$_{7/2}$	–	933.3	72.7

^{a}Binding energies referenced to a C 1s binding energy for graphite of 284.0 eV. ^{b}Full-width-half-maximum values (fwhm) given in parentheses. ^{c}The spin–orbit 2p$_{1/2}$ and 2p$_{3/2}$ components are separated by ~ 1.0 eV. The binding energy which is quoted corresponds most closely to that of the 2p$_{3/2}$ component.

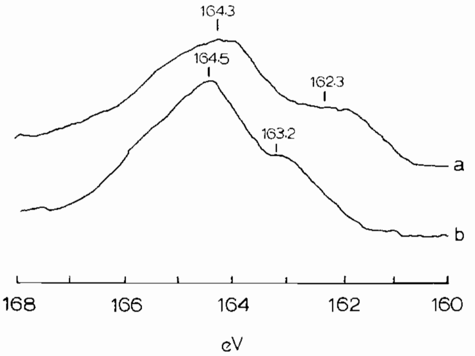


Fig. 1. Sulfur 2p binding energy spectra of (a) isoperthiocyanic acid and (b) $PtCl_2(L)_2$.

The infrared spectra of the complexes between 4000 and 400 cm^{-1} are somewhat unhelpful in elucidating the mode of coordination of the ligand. The data of Table I indicate that none of the ligand bands show significant changes in frequency on coordination to a metal. This would certainly seem to rule out coordination *via* the exocyclic amino-nitrogen atom since substantial frequency changes for the amino stretching, deformation and rocking modes are known to occur when primary amines are utilized as ligands. The ν(C=S) band also shows little change in frequency on coordination of the ligand to a metal and it could be concluded that this also excludes coordination *via* the exocyclic thione sulphur atom. However it has been established that such assignments are an oversimplification and the 'ν(C=S) band' is likely to be associated with a coupled vibration involving the C=S, C=N and C–N groups as well as to some extent the five-membered ring as a whole. Burns [16], for example, has shown for thiocarbohydrazide and thiosemicarbazide and their metal complexes, which in several cases are known to involve C=S→M bonding, that infrared bands which may be naively assigned to ν(C=S) are more correctly described as coupled vibrations involving C–N and C=S stretches as well as NCN and CNN bending motions. When such ligand bands do show shifts on coordination to a metal, they are not easily correlated with a particular bonding mode for the ligand.

Although the infrared spectra do not therefore point to a particular mode of coordination for the ligand, we believe that the X-ray photoelectron spectroscopic results we have obtained can reasonably be interpreted only in favor of bonding of the ligand *via* the exocyclic thione sulphur atom. While the C 1s and N 1s binding energies of the free ligand are not significantly affected upon coordination to copper(I) or platinum(II) (Table III), the chemical shift difference between the two sulphur sites decreases from 2.1 eV to ~1.3 eV on coordination (Table III and Fig. 1). Since the S 2p binding energy of the endocyclic disulphide sulphur atoms does not appear to change, whereas the related binding energy of the exocyclic thione sulphur shifts by +(0.6–0.9 eV) we believe that it is the latter donor site which binds the ligand to copper(I) and platinum(II). Support for this contention comes from the report that the S 2p binding energy of thiourea shifts by *ca.* +0.8 eV upon coordination [17].

The absence of 'shake-up' satellite structure associated with the Cu 2p binding energies of $CuCl(L)_2$ is consistent with its formulation as a complex of copper(I) [18].

Acknowledgements

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