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Metal Complexes of 2-Amino-5-nitrothiazole

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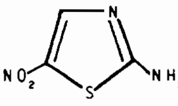
Abstract

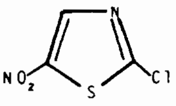
The preparation and characterisation of complexes of 2-amino-5-nitrothiazole (ANT) with Co(II), Ni(II), Cu(II), Cd(II), Cu(I) and Ag(I) are described. From spectral data it is inferred that the complexes fall into two groups: those in which ANT is bound through the ring nitrogen, and those in which the exocyclic amine group is bound to the metal ion. In the former group are complexes of the type $MCl_2(ANT)_2$ (M = Co, Ni, Cu, Cd); compounds containing methanol, $NiBr_2(ANT)_3(MeOH)$, $Ni(NCS)_2(ANT)_2(MeOH)_2$, $Ni(NCS)_2(ANT)_2(MeOH)$; and $AgNO_3(ANT)_2$, $Cu(AcO)_2(ANT)$ and $CuCl(ANT)_2$. In the latter group are complexes prepared from and containing N,N′-dimethylformamide: $CoSO_4(ANT)_2(DMF)_2$, $NiSO_4(ANT)_2(DMF)_2$, $NiCl_2(ANT)_2(DMF)_2$, $CuSO_4(ANT)(DMF)$ and $CuCl_2(ANT)(DMF)$. The probable structures of the nickel and cobalt complexes are discussed. The coordination chemistry of the thiazole group and the effect of the electron withdrawing nitro-group are discussed.

Introduction

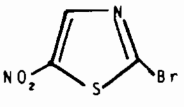
In this paper we describe studies on the metal complexes of thiazoles containing a nitro group at position 5: 2-amino-5-nitrothiazole (ANT) (I), 2-chloro-5-nitrothiazole (CNT) (II), 2-bromo-5-nitrothiazole (BNT) (III). These have several possible centres of coordination, the cyclic nitrogen, the nitro group, cyclic sulphur, π electrons of the ring and the exocyclic nitrogen in case of 2-amino-5-nitrothiazole.



(ANT)
I



(CNT)
II



(BNT)
III

Several antibiotics, such as althiomycine [1] and micrococcin [2, 3], contain a thiazole ring, as do many metabolic products of living organisms [4, 5], tomato [6], coffee [7, 8], roasted peanuts [9], the basic fraction of Scotch whiskey and Jamaica rum [10]. Thiazoles have also been separated from nitrogen bases of some petroleums [11].

The parmaceutical properties of 2-amino-5-nitrothiazole and related compounds have been tested [12–20]. Thus ANT, 0.07% in drinking water and 0.05% in feed, given to domestic cockerels at the appearance of teratomas induced by intratesticular injections of $ZnCl_2$, retarded tumor growth. Several Pt^{++} complexes of thiazole derivatives are found to be potential antitumour drugs [21–23]. The herbicidal and growth-regulating activity of some metal complex compounds of thiazole derivatives have been tested.

Coordination Complexes

Many studies have been carried out involving metal(II) complexes of simple and substituted thiazoles [e.g. 24–34]. Although coordination of thiazoles has little effect on ring geometry, it has been found that [28, 34–39] substituents in 2-, 4- and 5-positions modify the stoichiometries and stereochemistries of the complexes of cobalt(II), nickel(II), and copper(II). X-ray crystallographic data indicate that the structure of dichlorobis(thiazole)copper(II) [40] consists of infinite chains of doubly chloride-bridged copper(II) ions while bis-[dibromobis(4-methylthiazole)copper(II)] [41] is dimeric, with tetragonal-pyramidal geometry at each copper centre, and trans-dichlorobis(2,4-dimethylthiazole)copper(II) [42] is square planar and monomeric.

Thiazole forms complexes of the following types [24–42]: (i) $M(ClO_4)_2(t)_6$, (M = Co, Ni, Zn); (ii) $MX_2(t)_4$ (M = Co, X = Br, I, NCS; M = Ni, X = Cl, Br, I, NCS, ClO_4; M = Cu, Zn, X = NO_3, ClO_4); (iii) $MX_2(t)_2$ (M = Co, X = Br, I, NCS; M = Ni, X = Cl, Br, I, NCS, ClO_4; M = Cu, X = Cl, Br; M = Zn, X = Cl, Br, I); (iv) $MX_2(t)$ (M = Co, X = Cl, Br; M = Cu, X = Cl). With the exception of $CoI_2(t)$ and $CuCl_2(t)$ and possibly $Zn(ClO_4)(t)_4$, all other complexes are

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six coordinate in the solid state, bridging taking place when necessary. Polymeric octahedral structures have been assigned to the $MX_2(t)_2$ complexes where M = Co, Ni, Cu, X = Cl, Br. The structure, which consists of infinite chains of double halogen-bridged metal(II) ions, is reminiscent of those of the pyridine analogues, and is confirmed by three-dimensional X-ray structure analysis of dichlorobis-(thiazole)copper(II) complex [40].

2-aminothiazole and 2-bromothiazole are the substituted thiazoles which are best related to 2-amino-5-nitrothiazole, which is the subject of study in the present work. 2-amino-thiazole forms complexes of various stoichiometries with Ni(II), Co(II) and Cu(II) as well as with Sn(IV) and Ti(IV) [30, 32]. It has been suggested that with the two latter centres the exocyclic nitrogen coordinates; however, with the later transition metal ions, the situation is not clear-cut, and both ring nitrogen and amine nitrogen coordination have been suggested in the literature [23, 30–35].

2-bromo-thiazole forms complexes of the type ML_2X_2 (X = Cl, Br) with Co(II) and Cu(II), and has a low affinity for Ni(II). These complexes are similar to those of (AMT) of the same stoichiometry where the Co(II) complexes have distorted tetrahedral structures and the Cu(II) complexes are polymeric tetragonal [35]. The only reported transition metal complexes of 2-bromo-5-nitrothiazole (BNT) and 2-amino-5-nitrothiazole (ANT) are those with Pt(II) [23]. In $Pt(L_2)X_2$ (X = Cl, Br) it is suggested that with BNT coordination is through the ring nitrogen and with ANT through the amino group [23].

Coordination of thiazoles to transition metals has little effect on the geometry of the ring. Comparison of the bond distances in thiazole [43], with those in dichlorobis(thiazole)copper(II) [40]; and 2-amino-thiazole [44], with dichlorobis(2-aminothiazole)-copper(II) [45], respectively, suggests that while the effect of coordination on the geometry of thiazole is very insignificant (except for S(1)–C(2) bond distance), there is a slight decrease in the S(1)–C(2), C(5)–S(1) distances, and a slight increase in C(4)–C(5), C(2)–N(3), C(2)–N(6), and N(3)–C(4) bond distances.

This paper describes the preparation and characterisation of complexes of Co(II), Ni(II), Cu(II), Cd(II), Cu(I) and Ag(I). The Cu(II) complexes will be described in more detail in a subsequent publication.

Experimental

Materials and Manipulation

Reagent grade solvents and metal salts were used without further purification. Hydrated $Ni(NCS)_2$ was obtained by dissolving nickel(II) carbonate in thiocyanic acid. CuCl(I) was prepared by the addition of $CuCl_2$ to a solution of anhydrous sodium sulfite [46]. 2-Chloro-5-nitrothiazole was prepared by a Sandmeyer reaction from 2-amino-5-nitrothiazole [47, 48], 2-amino-5-nitrothiazole and 2-bromo-5-nitrothiazole (Aldrich Chemicals), were used after crystallization from methanol.

With the exception of $CuCl_4(HANT)_2$ and $Cu(AcO)_2(ANT)$ all the other complexes were very sensitive to air and moisture. Accordingly, experiments were carried out in all-glass Schlenk-type apparatus under an atmosphere of high purity nitrogen.

Physical Measurements

Infrared absorption spectra were obtained on Perkin-Elmer 457 instrument using samples in nujol mulls between NaCl plates, or as KBr pellets. Electronic spectra in acetone, DMF, MeOH, were recorded on a PE 124 instrument. Reflectance spectra in the range 4000–45 000 cm^{-1} were obtained with a Pye-Unicam SP700 instrument, using the SP735 reflectance attachment. Magnetic measurements were made over the temperature range 90K–360K on a Newport Instrument Gouy balance. Replicate determinations were made in most cases on separately prepared samples. The Gouy tube was calibrated with $HgCo(NCS)_4$. The calibration was checked by measuring the susceptibility of $Ni(en)_3S_2O_3$. Corrections for the diamagnetic portions of the molecule were obtained from Pascals' constants or by modifying the diamagnetic contributions of simpler molecules given in the literature. The value of μ_{eff} at each temperature was calculated using the equation

$$\mu_{eff} = 2.84[\chi_{m'} \times T]^{1/2}$$

where T is the absolute temperature, and $\chi_{m'}$ is the molar susceptibility corrected for diamagnetic effects and for TIP. The reciprocals of χ_m values corrected only for diamagnetism were plotted against temperature, and the best lines drawn. Whenever the straight lines so drawn intercepted the T axis at non-zero values, the T intercept, ϑ, was measured. Whenever appropriate μ was calculated using the relationship

$$\mu = 2.84[\chi_{m'}(T - \vartheta)]^{1/2}$$

where ϑ is the Weiss constant. At each temperature, measurements were performed at two different field strengths. The tube containing the samples was first heated and then gradually cooled.

Carbon-13 NMR spectra were recorded using a JEOL FX 90 Q Fourier Transform NMR spectrometer. Chemical shifts were obtained using Me_4Si as internal standard. X-ray diffraction powder photographs were recorded on a Philips Diffractometer PW1049 attached to a PW 1010 generator. An excitation voltage of 40 kV was used for Cu Kα radiation.

Preparation of ANT·HCl

ANT was slowly added to magnetically stirred concentrated hydrochloric acid until a white precipitate formed. Stirring was continued for another hour and the precipitate filtered off and dried in a dessicator.

Preparation of Complexes

$NiCl_2(ANT)_2$; $NiBr_2(ANT)_3(MeOH)_2$; $Ni(NCS)_2$-$(ANT)_2MeOH)_2$; $CuCl_2(ANT)_2$; $CdCl_2(ANT)_2$

These complexes were prepared by treating a concentrated solution of 2-amino-5-nitrothiazole (0.01 mol) in methanol with methanolic solution of the metal salts (0.01 mol). The resultant complexes were filtered off warm, washed twice with methanol and dried *in vacuo* at 60 °C. Changing metal to ligand ratio did not affect the composition of these complexes. When the solution containing the complex was cooled to 0 °C to enhance precipitation, the free ligand was obtained.

$CoCl_2(ANT)_2$

A concentrated solution of $CoCl_2 \cdot 6H_2O$ (0.01 mol) in methanol at 60 °C was treated with a methanolic solution of ANT (0.01 mol). The resultant green solution was evaporated at 40 °C to about one third, the yellow precipitate filtered off when warm, washed with methanol (about 20 ml) and dried *in vacuo* at 50 °C.

$CoCl_2(ANT)_2(MeOH)_2$

A solution of $CoCl_2$ (0.01 mol in 20 ml methanol) was slowly added to stirred solution of 2-amino-5-nitrothiazole (0.03 mol in 100 ml methanol) at 60 °C. A pink precipitate formed which was filtered off, washed with methanol and dried *in vacuo* at 60 °C.

$CuSO_4(ANT)(DMF)$; $CuCl_2(ANT)(DMF)$; $NiSO_4$-$(ANT)_2(DMF)_2$; $CoSO_4(ANT)_2(DMF)_2$; $NiCl_2$-$(ANT)_2(DMF)_2$

Warm concentrated solutions of metal salts in DMF were added to stirred concentrated solutions of ANT in DMF at 40 °C. The precipitates were filtered off, washed with 2 portions of methanol, and dried *in vacuo* at 80 °C. Metal to ligand ratios were always 1:1. Increasing the ligand to metal ratio to four times in the preparation of copper complexes, always gave the same product.

$Ni(NCS)_2(ANT)_2(MeOH)$

This complex was obtained in the tube used for magnetic measurements during the course of the experiment.

The tube was filled with $Ni(NCS)_2(ANT)_2(MeOH)_2$, heated to 363 K, subjected to two different magnetic fields, as previously described, the temperature was lowered at 20 K intervals to 100 K. At the end of the experiment a change in color from brown to green was observed. The IR, visible spectra and analytical data indicated that the second complex was $Ni(NCS)_2(ANT)_2(MeOH)$. Attempts to prepare this complex by prolonged heating at 363 K, or cooling at liquid nitrogen temperature were not successful. Prolonged exposure to different magnetic fields at 363 K or at 100 K did not affect the composition of $Ni(NCS)_2(ANT)_2(MeOH)_2$. The loss of one molecule of methanol took place only under the experimental conditions described above.

$[Cu(AcO)_2(ANT)]_2$

$[Cu(AcO)_2H_2O]_2$ was prepared *in situ* by adding copper powder to a solution consisting of 50% glacial acetic acid and 50% H_2O_2 at 100 °C. When the solution was dark blue, it was filtered to remove any unreacted copper powder, and the volume was reduced. When ANT was added to the dark blue solution, stirred at 60 °C, it turned green. The green crystals of $[Cu(AcO)_2(ANT)]_2$ precipitated after cooling.

$CuCl(ANT)_2$

CuCl (0.01 mol) and ANT (0.01 mol) in ether were stirred until all the ANT had reacted. The red precipitate which eventually came down was filtered off and dried *in vacuo*.

$AgNO_3(ANT)_2$

To a stirred solution of ANT (0.01 mol) in 50 ml acetone at 0 °C $AgNO_3$ crystals were added (0.0025 mol). The precipitate which formed after the solution was stirred for about 5 h was filtered off, washed with acetone, and dried *in vacuo*.

$CuCl_4(HANT)_2$

When concentrated HCl was slowly added to either a solution of $CuSO_4(ANT)(DMF)$ or $CuCl_2$-$(ANT)(DMF)$ in DMF, small shining green crystals precipitated. The crystals were washed with small amount of acetone and petroleum ether, and dried *in vacuo*.

Attempted Preparation of 2-bromo-5-nitrothiazole and 2-chloro-5-nitrothiazole Complexes

No complexes could be prepared using CNT and BNT, and the metal salts used in the preparation of 2-amino-5-nitrothiazole complexes. Other salts of the same metals including nitrates, bromides, iodides, sulphates, were also tested in several solvents, e.g., acetone, methanol, DMF, nitromethane with no positive results.

The compounds which were prepared are shown in Table I, together with analysis results.

TABLE I. Analytical Data for Complexes of ANT (Found (Calc)).

Compound	Analysis %		
	C	H	N
$CoCl_2(ANT)_2$	17.5	1.5	20.3
	(17.2)	(1.4)	(20.1)
$CoCl_2(ANT)_2(MeOH)_2$	19.7	2.8	17.9
	(19.9)	(2.9)	(17.4)
$CoSO_4(ANT)_2(DMF)_2$	19.7	3.0	15.5
	(19.3)	(2.7)	(15.0)
$NiCl_2(ANT)_2$	17.5	1.5	20.3
	(17.2)	(1.5)	(20.0)
$NiBr_2(ANT)_3(MeOH)$	16.9	1.9	18.0
	(17.5)	(1.9)	(18.3)
$Ni(NCS)_2(ANT)_2(MeOH)_2$	22.5	2.5	21.5
	(22.1)	(2.6)	(21.2)
$Ni(NCS)_2(ANT)_2(MeOH)$	21.6	2.0	22.4
	(21.7)	(2.0	(22.5)
$NiSO_4(ANT)_2(DMF)_2$	24.1	3.4	18.4
	(24.3)	(3.4)	(18.9)
$NiCl_2(ANT)_2(DMF)_2$	25.3	3.5	20.2
	(25.3)	(3.5)	(19.8)
$CuCl_2(ANT)_2$	17.2	1.4	19.7
	(17.0)	(1.4)	(19.8)
$CuSO_4(ANT)(DMF)$	19.5	2.7	14.9
	(19.1)	(2.7)	(14.8)
$CuCl_2(ANT)(DMF)$	20.5	2.7	15.9
	(20.4)	(2.8)	(15.9)
$Cu(AcO)_2(ANT)$	25.6	2.8	13.0
	(25.7)	(2.8)	(12.8)
$CuCl_4(HANT)_2$	14.5	1.4	17.0
	(14.5)	(1.4)	(16.9)
$CuCl(ANT)_2$	18.6	1.4	21.2
	(18.5)	(1.5)	(21.6)
$CdCl_2(ANT)_2$	14.9	1.3	17.4
	(15.2)	(1.3)	(17.7)
$AgNO_3(ANT)_2$	15.5	1.2	21.2
	(15.7)	(1.3)	(21.3)

TABLE II. Carbon-13 Chemical Shifts (ppm) for Thiazole and Substituted Thiazoles.

Compound	Solvent	C(2)	C(4)	C(5)
Thiazole[a]	DMSO	153.6	143.3	119.6
2-chlorothiazole[a]	DMSO	150.6	141.4	122.9
CNT	MeOH	156.6	141.6	149.1
	DMSO	157.9	142.9	150.8
	Acetone	164.1	150.3	157.2
2-bromothiazole[a]	DMSO	136.8	144.0	125.2
BNT	Acetone	113.2	176.4	114.1
2-aminothiazole[a]	DMSO	170.3	139.0	107.7
ANT	MeOH	175.1	146.4	138.0
	DMSO	173.5	147.2	135.4

[a] Data taken from ref. 49.

TABLE III. Effect of Nitro Substitution on the Carbon-13 Chemical Shifts (ppm). Spectra Measured in DMSO Solution.

Compound	$\Delta\delta^a$		
	C(2)	C(4)	C(5)
2-amino-5-nitrothiazole	+3.2	+8.2	+27.7
2-chloro-5-nitrothiazole	+7.3	+1.5	+27.9

[a] The positive sign indicates that chemical shifts are to higher fields.

Results

^{13}C NMR Results

The carbon-13 NMR spectra of substituted thiazoles were studied in order to probe the ground state electron distribution in this molecular framework, and to assess the relative contribution of the nitro substituent in determining this electron distribution.

The carbon-13 chemical shifts for 2-amino-5-nitrothiazole (ANT), 2-bromo-5-nitrothiazole (BNT), 2-chloro-5-nitrothiazole (CNT), are given in Table II. The assignments were made as follows. The most intense band in all cases, was assigned to C(4), because it is well known that the relaxation time, T_1 will be the shortest for this carbon due to dipole–dipole relaxation caused by the hydrogen atom attached to it. Assignments were aided by the comparison of spectra with the reported values [49] of 2-aminothiazole and 2-bromothiazole, and by the measurement of proton-coupled spectra.

In order to gain more insight into the effect of the nitro group on the perturbation of electron density at each carbon, the carbon 13 chemical shifts of CNT, BNT, and ANT were compared to the chemical shifts of 2-chlorothiazole, 2-bromothiazole, and 2-amino-thiazole, respectively. Table III contains the carbon-13 chemical shift difference, $\Delta\delta$, caused by the effect of the introduction of a nitro group at position 5 of the thiazole ring.

The chemical shift difference in 2-bromo-5-nitrothiazole is not included in Table III because the spectrum of the latter could not be recorded in DMSO and comparison of the shifts in two different solvents would not be meaningful, especially that the carbon-13 chemical shifts of the compounds concerned show some dependence on the solvents used.

As seen from Table III, the chemical shift difference, $\Delta\delta$, infuced by the nitro group at carbon-5 of the ring is nearly the same for 2-chloro-5-nitrothiazole and 2-amino-5-nitrothiazole, whereas it is quite different at positions 4- and 2- of the ring.

TABLE IV. Infrared Band Assignments (cm^{-1}) for ANT and its Complexes.

Compound	Assignment				
	νN–H	δNH_2	$\nu C-NO_2$	Ring stretching vibration	νC=S
ANT	3430, 3395, 3150, 3100	1623	1493	1507	738
$CoCl_2(ANT)_2$	3405, 3305, 3200, 3105	1617	1527	1480	735
$CoCl_2(ANT)_2(MeOH)_2$	3390, 3130, 3155, 3090	1605	1520	1500	738
$CoSO_4(ANT)_2(DMF)_2$	3280, 3080	1623	1536	1530	738
$NiCl_2(ANT)_2$	3405, 3305, 3200, 3110	1617	1525	1475	735
$NiBr_2(ANT)_3(MeOH)$	3300, 3155, 3100	1613	1520	1505	740
$Ni(NCS)_2(ANT)_2(MeOH)_2$	3465, 3400, 3295, 3215	1605	1535	1510	738
$Ni(NCS)_2(ANT)_2(MeOH)$	3400, 3160, 3173, 3120	1598	1531	1492	738
$NiCl_2(ANT)_2(DMF)_2$	3240, 3100	1623	1535	1507	738
$NiSO_4(ANT)_2(DMF)_2$	3280, 3080	1623	1535	1520	738
$CuCl_2(ANT)_2$	3415, 3300, 3200, 3115	1620	1532	1485	734
$CuCl_2(ANT)(DMF)$	3305, 3160, 3120	1623	1540	1512	737
$CuSO_4(ANT)(DMF)$	3300, 3120	1623	1560	1525	738
$Cu(AcO)_2(ANT)$	3370, 3285, 3193, 3117	1617	1527	1512	742
CuCl(ANT)	3440, 3340, 3240, 3100	1598	1520	1490	734
$CdCl_2(ANT)_2$	3415, 3315, 3200, 3100	1620	1525	1490	734
$AgNO_3(ANT)_2$	3390, 3280	1623	1530	1472	738

Infrared Spectra

The infrared spectra of all the complexes showed a number of differences from the spectra of the free ligand (Table IV) principally in regions associated with the NH_2 group, the nitro group, and the ring vibrations. The spectra of the complexes in nujol or as KBr pellets were compared with the spectrum of ANT in solid state. The infrared spectrum of ANT showed four bands in the ν(N–H) stretching frequency region. The presence of four bands in this region instead of the usual two bands associated with amine NH stretching vibrations implies the existence of various types of –N–H bonds, which could result from intermolecular or intramolecular donor–acceptor interactions among the various coordination sites present in ANT. The infrared spectra of all complexes, with the exception of those containing DMF, retained the four bands associated with νNH which were shifted to lower frequencies.

In the spectra of mixed DMF complexes, the band associated with the carbonyl absorption νC=O, which is at 1675 cm^{-1} in the spectrum of DMF is shifted to lower frequencies by 20–40 cm^{-1} in all cases, indicating the coordination of DMF to the central metal ion.

The presence of MeOH in the mixed methanol complexes is shown by the presence of the characteristic bands associated with –O–H bending at *ca.* 1460 cm^{-1} and C–O stretching vibration near 1010 cm^{-1}, while its coordination to the central metal ion is inferred because the O–H bending frequency is shifted to lower regions, and prolonged heating at 90 °C did not effect the spectra of the mixed methanol complexes.

Electronic Spectra

In the reflectance spectra of all complexes, any bands of wavenumbers higher than 18 000 cm^{-1} could not be assigned with any certainty because of the presence of a very broad, and intense absorption in the ultraviolet region. Bands at lower wavenumbers are listed in Table V, (Figs. 1–4).

The solution electronic spectra of all the complexes indicated dissociation, which probably resulted from the low basicity of ANT and the steric hindrance caused by the substituents. The solvents tried included acetone, methanol, ethanol, water, and DMF.

TABLE V. Electronic Spectra (cm^{-1}) (Solid State Diffuse Reflectance Spectra).

Compound	Band maxima
$CoCl_2(ANT)_2$	6300, 14700, 18000
$CoCl_2(ANT)_2(MeOH)_2$	7300, 14500(sh), 18700
$CoSO_4(ANT)_2(DMF)_2$	8000, 14700, 18800(sh), 19500
$NiCl_2(ANT)_2$	7300, 13200
$NiBr_2(ANT)_3(MeOH)$	7300, 8800, 12500, 14200
$Ni(NCS)_2(ANT)_2(MeOH)_2$	8500, 10500, 14000, 16500
$Ni(CNS)_2(ANT)_2(MeOH)$	9200, 15700
$NiSO_4(ANT)_2(DMF)_2$	8300, 14800
$NiCl_2(ANT)_2(DMF)_2$	8000, 14000
$CuCl_2(ANT)_2$	13500
$CuSo_4(ANT)(DMF)$	11000
$CuCl_2(ANT)(DMF)$	14200
$Cu(AcO)_2(ANT)$	13900
$CuCl_4(HANT)_2$	13900

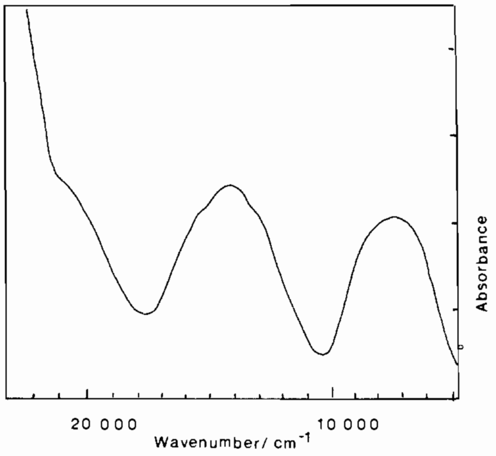


Fig. 1. Reflectance spectrum of $NiCl_2(ANT)_2$.

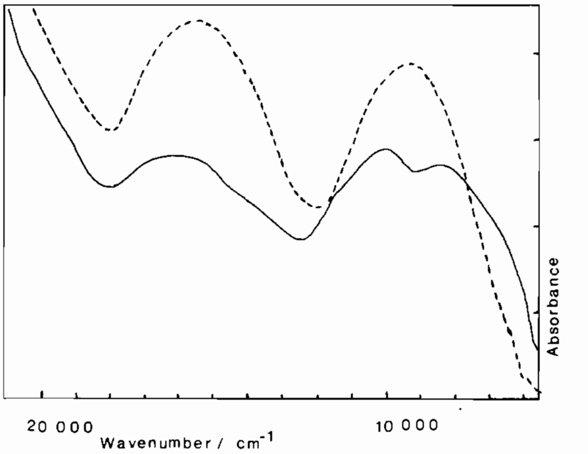


Fig. 2. Reflectance spectra of $Ni(NCS)_2(ANT)_2(MeOH)_2$ (——); and $No(NCS)_2(ANT)_2(MEOH)$ (- - -).

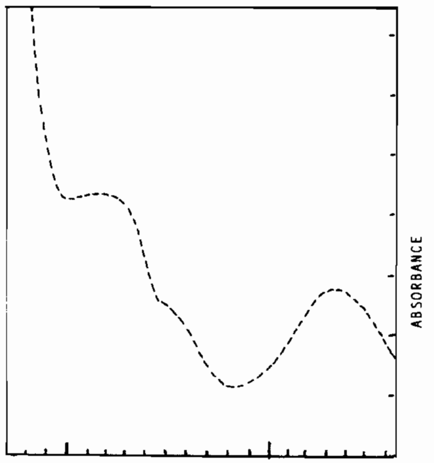


Fig. 3. Reflectance spectrum of $CoCl_2(ANT)_2$.

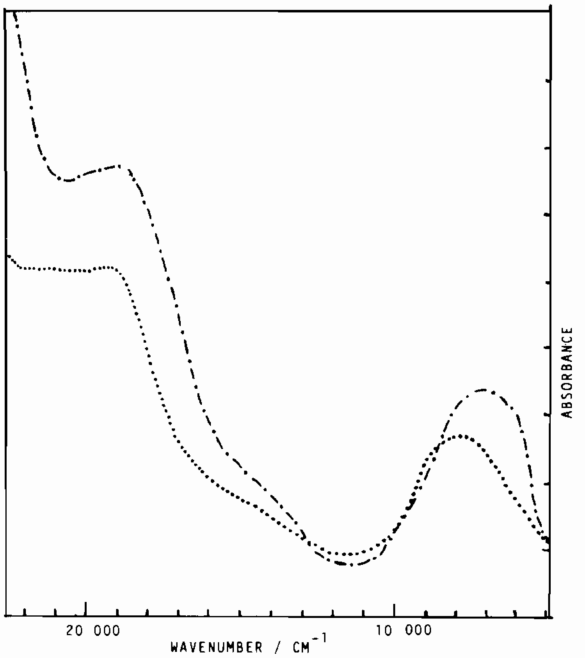


Fig. 4. Reflectance spectra of $CoCl_2(ANT)_2(MeOH)_2$ (— — —); and $CoSO_4(ANT)_2(DMF)_2$ (· · ·).

X-ray Diffraction Powder Photographs

The X-ray diffraction powder photographs of $NiCl_2(ANT)_2$, $CuCl_2(ANT)_2$, $CoCl_2(ANT)_2$ and $CdCl_2(ANT)_2$ were compared to find out if they are isomorphous. One-to-one correspondence in the number of peaks, and in spacings and intensities was found only for the Cu^{2+} and Co^{2+} complexes, indicating that these two complexes are isomorphous.

Magnetic Susceptibility Measurements

Nickel(II) complexes [50, 51]

The temperature independent paramagnetism *TIP*, was calculated from the relationship

$$TIP = 8N\beta^2/\Delta \cong 2.09/\Delta \text{ c.g.s.u.}$$

where Δ is the energy of the level $^3T_{2g}$ being mixed into the ground state, and amounts to almost 7% of the room temperature susceptibility in these complexes. The values of *TIP*, the diamagnetic correction, and θ are given in Table VI.

The plots of $1/\chi_m$ (where χ_m is corrected for diamagnetism) *vs.* temperature for all the Ni(II) complexes with the exception of $NiCl_2(ANT)_2$, gave straight lines passing through the origin.

The plot of $1/\chi_m$ *vs.* temperature for the $NiCl_2(ANT)_2$ complex gave a straight line which intersected the T axis at $\theta = 24$ K indicating possible ferromagnetic interaction between the Ni(II) ions. The variation of μ_{eff} with temperature is shown in Table VII where it is shown to range from 3.39 to

TABLE VI. Some Spectral and Magnetic Parameters.

Compound	Δ (cm^{-1})	Diamagnetic correction × 10^6 (c.g.s.u.)	*TIP* × 10^6 (c.g.s.u.)	θ (K)	μ (BM)
$NiCl_2(ANT)_2$	7300	176.36	286.3	24 ± 1	3.29[a]
$NiBr_2(ANT)_2(MeOH)$	8300	231.07	251.8[b]	0	3.14
$Ni(NCS)_2(ANT)_2(MeOH)_2$	9040	258.18	231.2[b]	0	3.20
$Ni(NCS)_2(ANT)_2(MeOH)$[c]	9200	[c]	227.2	0	3.18
$NiCl_2(ANT)_2(DMF)_2$	8000	265.6	261.2	0	3.20

[a] See text. [b] The value of *TIP* was calculated by using the weighted mean of the two components of the split band as a measure of the energy of the unsplit band, Δ, in the relationship: $TIP = 8N\beta^2/\Delta \cong 2.09/\Delta$ c.g.s.u. [c] See discussion.

TABLE VII. Magnetic Moments of some ANT Complexes.

$NiCl_2(ANT)_2$		$CoCl_2(ANT)_2$[a]		$CoSO_4(ANT)_2(DMF)_2$	
T (K)	μ_{eff} (BM)	T (K)	μ_{eff} (BM)	T (K)	μ_{eff} (BM)
363.16	3.39	363.16	4.38	363.16	5.21
343.16	3.38	343.16	4.34	343.16	5.20
323.16	3.38	299.16	4.36	323.16	5.19
299.16	3.41	283.16	4.37	299.16	5.17
283.16	3.42	243.16	4.36	283.16	5.16
263.16	3.44	223.16	4.34	263.16	5.17
243.16	3.46	183.16	4.34	243.16	5.15
223.16	3.47	143.16	4.30	223.16	5.14
203.16	3.49	103.16	4.25	203.16	5.09
183.16	3.51	91.16	4.22	183.16	5.06
163.16	3.54			163.16	4.99
143.16	3.59			143.16	4.97
123.16	3.65			123.16	4.78
103.16	3.74			91.16	4.70

[a] $\theta = -10$ K.

3.74 BM. The value of the magnetic moment for this compound shown in Table VI was calculated from the relationship (where $\chi_{m'}$ is corrected for both diamagnetism and *TIP*).

$$\mu = 2.84[\chi_{m'}(T - \theta)]^{1/2}$$

The magnetic moment (3.29 BM) corrected for ferromagnetism in this way, was used to calculate the value of spin-coupling constant (λ) from the relationship

$$\mu = 2.83(1 - 4\lambda'/\Delta)$$

and was found to be 297 cm^{-1}.

Cobalt(II) complexes

In octahedral cobalt(II) the ground state is $^4T_{1g}$ and a large orbital contribution to the moment is expected. Mixing in of a singlet excited state lowers the moment but a value in excess of 5 BM is expected. The ground state for tetrahedral cobalt(I) is $^4A_{2g}$ and a low moment is usually obtained. An excited triplet state is comparatively low in energy and can be mixed with the ground state. Moments in the range of 4–5 BM have been predicted and are found experimentally [51, 52].

The *TIP* term is not included in the calculations of effective magnetic moments of these complexes due to the uncertainty involved in the reflectance spectral bands at high energies. However, the relative effect of *TIP* is not large in complexes with three unpaired electrons. The variation in μ_{eff} with temperature is shown in Table VII.

Discussion

The Donor Centre in 2-amino-5-nitrothiazole

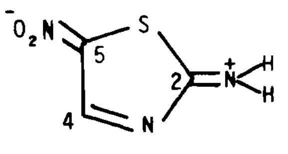
2-Amino-5-nitrothiazole (ANT) have five possible centres of coordination: cyclic sulphur, the nitro group, electrons of the ring, the exocyclic nitrogen, and cyclic nitrogen.

Previous work on simpler thiazoles, such as unsubstituted thiazole, alkyl and halogen substituted thaizoles has indicated that with the exception of one case, where sulphur coordination is proposed [39], substitution is through ring nitrogen [24, 28, 29, 40]. For the 2-amino metal complexes both ring nitrogen and exocyclic nitrogen coordination is suggested [30–35]. The authors proposing amino nitrogen coordination have based their arguments on the fact that steric hindrance at the ring nitrogen, caused by the amino group, would favour the coordination of the latter group. However, recent X-ray crystallographic data on dichlorobis(2-aminothiazole)cobalt [45], clearly indicates that coordination is though ring nitrogen in this complex. Doradrio *et al.* have proposed amino nitrogen coordination for the only transition metal complex of ANT so far reported in the literature [23].

In the infrared spectra of all the complexes studied in this work, no significant change was observed in the νC=S vibrations, thus eliminating the possibility of sulphur coordination.

The small values of Δ observed in the reflectance spectra (Tables V and VI) indicate that coordination through the nitro group is unlikely [53].

The carbon-13 chemical shift difference, $\delta\Delta$, between 2-aminothiazole and 2-amino-5-nitrothiazole shows a deshielding effect of 3.2 ppm, 8.2 ppm, and 27.7 ppm at C(2), C(4), and C(5), respectively. This deshielding effect may be explained if resonance form (**IV**) makes a substantial contribution to the ANT hybrid. In this form (**IV**), the strong electron-withdrawing resonance effect of the nitro group is capable of delocalising the electron density away from the ring.



IV

The deshielding effect at C(2) could be explained by further enhancement in the double bond character of C(2)–NH_2, which is present in 2-aminothiazole. Thus, the conjugation of the nitro group with the present system will make the amino nitrogen even less basic than in 2-aminothiazole. This result is in line with previous results obtained by conformational studies by dynamic NMR on 2-NN-dimethylaminothiazole, and 5-nitro-2-NN-dimethylaminothiazole [54] that predict an enhancement in Ar–N double bond character in the latter compound.

Although a reduction in the basicities of the ring and amino nitrogens is predicted, there is no clear indication as to which one of the two is affected more by the introduction of a nitro group. The protonation of ANT in solution has been studied by UV spectroscopy [55] and pK_a measurements on a number of 5-substituted 2-aminothiazoles [56]; and in both cases ring nitrogen protonation is proposed.

The infrared spectrum of protonated ANT in solid form, which was prepared in this work, does not produce conclusive evidence to the site of protonation. The band at 3220 cm^{-1} falls in the range associated with primary amine stretching frequency, while the band at 1595 cm^{-1} is typical for $-NH_3^+$ absorption, because $\geqslant\overset{+}{N}H$ does not absorb in this region. The two closely located bands at 1635 cm^{-1} and 1648 cm^{-1} were assigned to δNH_2 and $-NH_3^+$ absorption, respectively.

The infrared spectra of all complexes showed a shifting to lower frequencies in $\nu_s NH$ and $\nu_a NH$ regions. This may result from the coordination of the amine group, it might also be due to the electronic effects resulting from other coordination sites, or hydrogen bonding of NH_2 to other groups.

The coordination of $-NH_2$ nitrogen results in a shift to lower frequencies in $\nu_a NH$ and $\nu_s NH$, a shift to higher frequencies in δNH_2 and no shift or slight shift in the ring stretching vibration [33].

The presence of four bands corresponding to $\nu_s NH$ and $\nu_a NH$, is evident in the infrared spectra of all complexes with the exception of the spectra of mixed DMF complexes, which show only two bands in this region. The presence of more than the usual two bands associated with amine stretching vibration is probably due to the existence of dissimilar N–H bonds in these complexes, these could result from (i) hydrogen bonding of the NH_2 group with either the anions, or solvents, or the nitro groups; or (ii) some type of intermolecular donor–acceptor interaction between the amino group and the nitro group; or (iii) the bridging of the ligand via NH_2 to another metal ion. The predominance of structure (**IV**) results in the reduction of the donor strength of the amine nitrogen, and thus leaves the ring nitrogen as the potential coordinating site. The negative shifts in δNH_2 vibrations further support this type of interaction.

The spectra of mixed DMF complexes show two bands corresponding to $\nu_s NH$ and $\nu_a NH$. An exception is the spectrum of $CuCl_2(ANT)(DMF)$ which shows three bands in this region. Another important feature of these spectra is the very significant negative shift in the frequencies of the latter bands as compared to the slight shifts in the spectra of ring nitrogen coordinated complexes discussed above. The band associated with δNH_2 or $\delta N–H$ is not clearly seen due to the presence of $\nu C=O$ vibration of DMF in the same region, however no band is seen below the δNH_2 vibration of the free ligand indicating that all δNH_2 shifts are to higher frequencies, as expected for amine coordinated complexes.

Thus based on the infrared spectral evidence, the complexes prepared could be divided into two groups: Group (A), which has ring-nitrogen bonded ANT; and Group (B), which has amine bonded ANT (Scheme 1).

Group (A)	Group (B)
$MCl_2(ANT)_2$ (M = Co, Ni, Cu, Cd)	$CoSO_4(ANT)_2(DMF)_2$
$CoCl_2(ANT)_2(MeOH)_2$	$NiSO_4(ANT)_2(DMF)_2$
$NiBr_2(ANT)_3(MeOH)$	$NiCl_2(ANT)_2(DMF)_2$
$Ni(NCS)_2(ANT)_2(MeOH)_2$	$CuSO_4(ANT)(DMF)$
$Ni(NCS)_2(ANT)_2(MeOH)$	$CuCl_2(ANT)(DMF)$
$AgNO_3(ANT)_2$	
$Cu(AcO)_2(ANT)$	
$CuCl(ANT)_2$	

Scheme 1.

If the ring nitrogen can behave as the donor atom, the question should be asked as to why 2-chloro-5-nitrothiazole (CNT) and 2-bromo-5-nitrothiazole (BNT) do not form similar complexes.

Theoretical treatment [57] of 2-aminothiazole, 2-chlorothiazole, and 2-bromothiazole predicts a lower electron density at ring nitrogen for the last two molecules. In fact 2-bromothiazole forms complexes of the type MX_2L_2 (M = Cu, Co; X = Cl, Br) only, whereas, 2-aminothiazole forms, in addition to complexes of the type $MX_2 \cdot L_2$, complexes where foure ligands are coordinated to one metal ion for the same metal salts (MX_2L_4) implying the higher basicity of the donor site in the latter. Consequently, the introduction of a nitro group, as indicated by ^{13}C NMR results, will make the ring nitrogen in CNT and BNT less basic than in ANT and would result in further reduction in σ-donor strength of the former two molecules.

Discussion of the Structures

Complexes of the type $MCl_2(ANT)_2$ (M = Ni, Co, Cu, Cd)

Infrared evidence indicates that all these compounds have the ANT moiety coordinated to the metal via the ring nitrogen, however they are not all isomorphous. X-ray diffraction measurements show that the Co^{2+} and Cu^{2+} complexes are isomorphous. These compounds appear to be five coordinate dimeric, like $CuBr_2$(4-methylthiazole)$_2$ [41]. Consideration of the steric factors involved might lead to the conclusion that the $MCl_2(ANT)_2$ complexes should be monomeric, that $CuCl_2$(2,4-dimethylthiazole)$_2$ [42]. However, spectroscopic and magnetic evidence indicates penta coordination for both the cobalt and nickel complexes. The copper complex will be discussed in detail in a subsequent paper.

The infrared and ultraviolet spectra of $CdCl_2(ANT)_2$ are almost identical to those of the nickel analogue, $NiCl_2(ANT)_2$. The significant differences in X-ray powder patterns of the two complexes can therefore be related to the sizes of the Ni^{2+} and Cd^{2+} ions, and similar octahedral structures are proposed for both compounds.

$NiCl_2(ANT)_2$

The reflectance spectrum of $NiCl_2 \cdot (ANT)_2$ (Table V, Fig. 1) is typical of a slightly distorted octahedral complex with a weak ligand field. The spectra are similar to those of $Ni(t)_4Cl_2$ [27], $Ni(t)_2Cl_2$ [24], and in particular Ni(quinoline)$_2$Cl$_2$ [58]. Like quinoline, ANT is sterically hindered and produces a relatively weak ligand field with small band splittings, so that the ν_1, 7300 cm^{-1} ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ in O_h) and ν_2 13200 cm^{-1} ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ in O_h) bands are broad, but the splittings are not clearly defined. Thus the structure is essentially octahedral, with *trans* ANT ligands. The octahedron is completed by chloride bridges, leading to a polymeric species (Fig. 5).

The magnetic moment of 3.29 BM at room temperature (Table VI) is in the range found for similar structures [58]. The value (24 K) is slightly larger than that found for the quinoline analogue (19 K) [58].

$CoCl_2(ANT)_2$

This complex has been shown to be isomorphous with the copper analogue, $CuCl_2(ANT)_2$. There are bands in the visible absorption spectrum at 6300 cm^{-1}, 14700 cm^{-1} and 18000 cm^{-1} (Fig. 3). It has been suggested [59–61] that Co(II) complexes with coordination number 5 have spectral bands in the regions 5000–6500 cm^{-1} and 14000–16000 cm^{-1}. Complexes with square pyramidal rather than trigonal bipyramidal geometry, typically have their lowest energy band shifted to the high end of the 5000–6500 cm^{-1} region [59, 62]. The complex exhibits Curie–Weiss behaviour (Table VII). Magnetic and spectral data are very similar to those of the pentadentate cobalt(II) complex of a Schiff base ligand CocbpN reported by Boge *et al.* [62]. However, the situation is not unambiguous. The ESR spectrum of the isomorphous copper analogue is consistent with a number of other possibilities*. If these complexes are pentadentate then chloride bridging of the type found [41] in bis[dibromo bis(4-methylthiazole)copper(II)] is the most like type of structure.

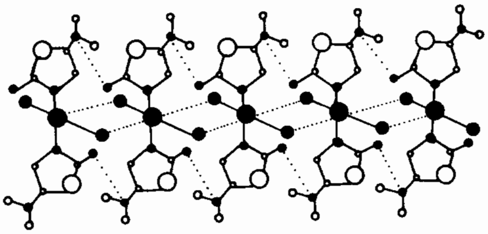


Fig. 5. Proposed structure of $NiCl_2(ANT)_2$.

Metal(I) Complexes

$AgNO_3(ANT)_2$ and $CuCl(ANT)_2$

The infrared spectrum of $AgNO_3(ANT)_2$ exhibits the characteristic bands for nitrate ion bonded to a metal ion. The bands at 824 cm^{-1}, 1040 cm^{-1}, and 1330 cm^{-1} are three of the five characteristic bands associated with the nitrate ion, the other two being masked by the ligand bands. The reflectance spectra of these two complexes show a remarkable increase in the intensities of the bands in the region 20000–30000 cm^{-1}, which could be attributed to an interaction between the metal(I) ions and a π-acceptor.

Mixed Methanol M(II) Complexes

$NiBr_2(ANT)_3(MeOH)$

The electronic spectrum of this complex is typical of a tetragonally distorted octahedral species, with D_{4h} symmetry and a $^3B_{1g}$ ground state. The bands

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*The ESR spectrum of powdered $CuCl_2(ANT)_2$ gave three g values at 2.054, 2.131 and 2.205. These values will be discussed in a subsequent paper; however, the following are possible: elongated rhombic octahedral, rhombic square planar, distorted-based pyramidal, elongated axial with slight misalignment of principal axes.

may be assigned as follows: $^3B_{1g} \rightarrow {}^3B_{2g}$ (7300 cm^{-1}), $^3B_{1g} \rightarrow {}^3E_g$ (8800 cm^{-1}), $^3B_{1g} \rightarrow {}^3A_{2g}$ (12 500 cm^{-1}), $^3B_{1g} \rightarrow {}^3E_g(F)$ (14 200 cm^{-1}). The magnetic moment at room temperature is 3.14 BM and $\theta = 0$. We assume, therefore, that the complex is tetragonal and monomeric. The infrared spectrum shows that the methanol is coordinated, but how the six ligands are distributed in the coordination sphere is not known.

$Ni(NCS)_2(ANT)_2(MeOH)_2$ and $Ni(NCS)_2(ANT)_2(MEOH)$

It was noticed that after the magnetic susceptibility measurement experiment following the procedure described in 'Experimental', the color of $Ni(NCS)_2(ANT)_2(MeOH)_2$ had changed from brown–yellow to bright green. Elemental analysis suggested the loss of one molecule of methanol. Such behavior is not unusual for $Ni(NCS)_2$ complexes. In thermal analysis of $Ni(SCN)_2(pyridine)_4$ [63], the formation of the intermediate $Ni(SCN)_2(pyrdine)_2$, was detected. On the basis of the information obtained from the derivatogram, $Ni(SCN)_2(pyrdine)_2$, was prepared by heating a sample to a temperature corresponding to the horizontal section of the TG curve [64], and by 'freezing in' the reaction by rapidly removing the furnace. It was found that $Ni(SCN)_2(pyridine)_2$, contained thiocyanate bridges, while in $Ni(SCN)_2(pyrdine)_4$ the SCN was N-bonded as the isothiocyanate complex. The magnetic moment of the original complex and the thermal decomposition product were identical (3.10 and 3.12 BM, respectively) excluding the possibility of extensive stereochemical rearrangement during thermal decomposition.

Prolonged heating of a sample of $Ni(NCS)_2(ANT)_2(MeOH)_2$ in the tube used for magnetic measurement, at 100 °C, did not change its composition, nor did repeating the magnetic susceptibility experiment first by heating to 90 °C and then rapidly cooling to liquid nitrogen temperature bring about any change; however, repeating the experiment under the conditions described gave the same result. Consequently, it seems that the change occurred either because of the slow rate of cooling or due to the combined effect of cooling and the magnetic field. The magnetic moment of the green product, calculated by using the molecular mass of $Ni(NCS)_2(ANT)_2(MeOH)_2$ and the diamagnetic correction associated with it, was found to be constant at 3.20 ± 0.05 BM. The fact that there was no change in the weight of the tube, because the tube was sealed, makes this value quite reasonable. Such a case is reported for (Cu_3Br_3 guaninium. nH_2O) [65] and is ascribed to slight changes in the lattice which change the Cu–Br–Cu angle and where the delocalisation properties of the bridging ligand to just compensate for the expected decrease in the moment.

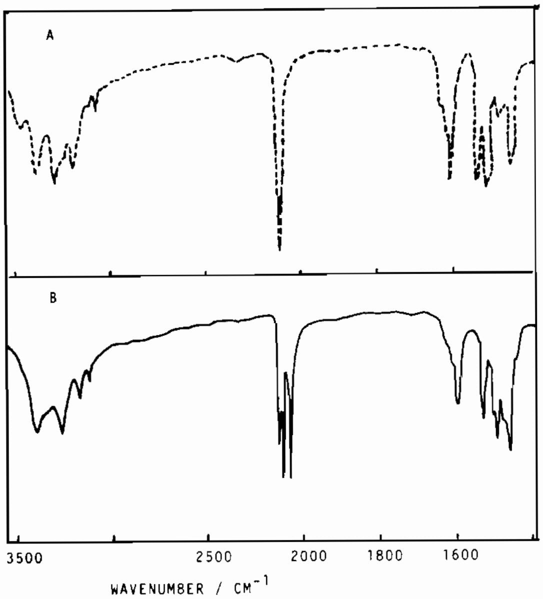

Fig. 6. Infrared spectra: A, $Ni(NCS)_2(MeOH)_2$; B, $Ni(NCS)_2(ANT)_2(MEOH)$, (as KBr pellets).

The infrared spectrum (Fig. 6) shows that the C–N stretching mode for $Ni(NCS)_2(ANT)_2(MeOH)_2$ is at 2107 cm^{-1}, and the band at 818 cm^{-1} assigned to C–S stretch is in the region expected for an N-bonded isothiocyanate [66]. In the IR spectrum of the green $Ni(NCS)_2(ANT)_2(MeOH)$, the C–N band is split into three bands at 2125, 2105 and 2072 cm^{-1}; indicating that there has been a change in the coordination of the NCS groups on losing the methanol from the coordination sphere.

The diffuse reflectance spectrum of the dimethanolo complex in the visible region (Fig. 2) shows considerable splitting of the bands, showing tetragonal distortion D_{4h} from octahedral (Oh) symmetry (Table V). The bands can be assigned as follows: $^3B_{1g} \rightarrow {}^3B_{2g}$ (8500 cm^{-1}); $^3B_{1g} \rightarrow {}^3E_g$ (10 500 cm^{-1}); $^3B_{1g} \rightarrow {}^3A_{2g}(F)$ (14 000 cm^{-1}) and $^3B_{1g} \rightarrow {}^3E_g(F)$ (16 500 cm^{-1}). The splitting is thus larger than in the tetragonal $NiBr_2(ANT)_3(MeOH)$. The band positions are very similar to those reported for substituted aniline complexes of the type $Ni(An)_2(NCS)_2$ [67], which were assigned tetragonal polymeric structures, with *trans* aniline groups and bridging thiocyanate groups. In these complexes, however, the infrared spectra clearly showed the presence of bridging SCN-groups. The ANT complex shows the presence of coordinated methanol, one of which is lost to give the green product. The electronic spectrum of the green product is typical of an octahedral species (Fig. 2) and the infrared spectrum (Fig. 6) shows that the N–C band is split. Both compounds obey the Curie Law, showing that if bridging occurs, then there is little interaction between the metal ions.

$CoCl_2(ANT)_2(MeOH)_2$

The reflectance spectrum of this complex consists of two bands at about 7300 and 18 700 cm^{-1}. For octahedral cobalt(II) complexes three bands are expected corresponding to the three spin-allowed transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2), $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3). However, the transition $^4T_{1g} \rightarrow {}^4A_{2g}$ corresponds to a two-electron jump and has a much lower oscillator strength than the other two bands and will be much weaker [68]. The band at 7300 cm^{-1} can therefore be assigned to the ν_1 transition and the band at 18 700 cm^{-1} to the ν_3 transition, and the weak shoulder at about 14 500 cm^{-1} could be assigned to ν_2 transition.

Mixed DMF Metal(II) Complexes

$NiCl_2(ANT)_2(DMF)_2)$

The constant magnetic moment of this complex $\mu = 3.20$ BM, and the reflectance spectrum indicate its octahedral nature, each nickel(II) ion being surrounded by two ANT, two DMT molecules and two chloride ions. The bands in the visible region may be assigned as $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ at 8000 cm^{-1} and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ at 14000 cm^{-1} in O_h symmetry.

$NiSO_4(ANT)_2(DMF)_2)$

The infrared spectrum of this complex shows four bands at 983 cm^{-1}, 1045 cm^{-1}, 1075 cm^{-1} and 1153 cm^{-1} suggesting that the symmetry of the $SO_4{}^{2-}$ ion is reduced to C_{2v}, characteristic of bidentate $SO_4{}^{2-}$ ion.

The reflectance spectrum suggests that this complex had octahedral geometry. The bands ν_1 and ν_2 correspond to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, at 8300 cm^{-1} and 14800 cm^{-1}. The calculated Δ of 811 cm^{-1} is in good agreement with that obtained from ν_1 (830 cm^{-1}).

$CoSO_4(ANT)_2(DMF)_2)$

The reflectance spectrum of this complex is similar to that of the violet isomer of Co(pyridine)$_2$-Cl_2 in which the cobalt is six-coordinate [69]. By analogy with the band assignments of Ferguson, the bands at about 18 800 and 19 500 cm^{-1} arise from $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition which is split in complexes of D_{4h} symmetry or lower. The low intensity band at 14 700 cm^{-1} arises from the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition, and the band at 8000 cm^{-1} arising from the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$. The infrared bands at 980 cm^{-1} 1045 cm^{-1}, 1112 cm^{-1} and 1155 cm^{-1} indicate that the sulphate ion is bidentate assuming C_{2v} symmetry. The room temperature magnetic moment at 5.17 BM and the remarkable decrease in the moment with decreasing temperature (Table VII) are consistent with the proposed structure.

Conclusions

The deshielding effect of the nitro group observed in the carbon-13 NMR spectra of 2-chloro-5-nitrothiazole and 2-amino-5-nitrothiazole, the lack of formation of Ni(ANT)Cl_2 complex (where ANT is bridging like the corresponding 2-aminothiazole complex), and the failure to prepare complexes with BNT and CNT, clearly indicate considerable reduction in the electron density in the donor sites of these ligands.

The formation of halogen bridged, mixed MeOH complexes and the lack of formation of complexes of higher ligand to metal ratio could be the result of ring nitrogen bonded ANT being a better π-acceptor than a σ-donor, bridging and coordination of methanol providing a means for maintaining the effective electroneutrality on the central ion.

Unlike 2-aminothiazole, ANT did not form complexes in MeOH or DMF with Co(II) bromide, Ni(II) iodide or Cu(II) bromide. The lack of ring nitrogen coordinated complexes in methanol could be explained as follows. It is known that the basicities of the three anions follow the sequence $Cl^- > Br^- > I^-$, whereas the π-accepting ability of these anions is in the reverse order [70]. Thus, electron transfer to ANT decreases along the series, $Cl^- > Br^- > I^-$, thus making formation of these complexes unlikely. To explain the lack of formation $-NH_2$ coordinated complexes with these metals, consideration of basicities and π-acceptor properties alone could not be enough, because DMF is also a π-acceptor, yet $-NH_2$ coordinated complexes are formed in its presence. Therefore, two additional factors should be considered, (a) the solvating properties of DMF, (b) the hard/soft relations between ANT and the metal ions.

DMF solvates cations better than anion [71]. Therefore, with ligand sites being occupied by DMF molecules, there will be little room for the sterically hindered ring nitrogen to form bonds with the metal centres. It is also known that DMF has a mild preference for solvating large anions which function as soft bases, such as Br^-, I^-, and NCS^-, thus reducing their basicity needed for achieving electroneutrality at the central metal ion [71]. Further, the dipolar aprotic solvent DMF will interact with the polar ANT, by breaking the donor–acceptor intermolecular interaction between the nitro group and amine group, thus reducing the electron-withdrawing character of the nitro group, liberating the amine group and making it more available for bonding.

In the ligand ANT, the various possible coordination sites present a range of hard and soft donors. The expected order of hardness is as follows:

Nitro-group > amine nitrogen > ring nitrogen > sulphur > ring electrons. In the complexes prepared in this work, amine coordination takes place in the $CoSO_4$, $NiSO_4$, $NiCl_2$, and $CuCl_2$, and only with the assistance of DMF.

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