Complexes of Manganese(II), Iron(II), Cobalt(II), and Nickel(II) with the New α,α′,α″-Tri-imine, 2,6-(Dibenzothiazol-2-yl)pyridine

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The new α,α′,α″-tri-imine, 2,6-(dibenzothiazol-2-yl)pyridine (N–N–N), has been prepared and its structure has been confirmed by its mass spectrum. The mono-ligand complexes $M(N–N–N)Cl_2$ (M = Mn, Fe, Co, Ni), $M(N–N–N)X_2$ (M = Fe, Co; X = Br, NCS), $Fe(N–N–N)I_2$, and $M(N–N–N)(NO_3)_2$ (M = Co, Ni) have been obtained. Spectral data indicate that the iron and cobalt complexes (where X = Cl, Br, I, or NCS) are five-co-ordinate but the complexes $M(N–N–N)(NO_3)_2$ (M = Co, Ni) and $Ni(N–N–N)Cl_2$ are octahedral. The manganese complex may be either five- or six-co-ordinate. All the complexes are spin-free and have normal magnetic moments.

The bis-ligand complexes $[M(N–N–N)_2](ClO_4)_2,nH_2O$ (M = Fe, Co), $[Co(N–N–N)_2](BF_4)_2,4H_2O$, and $[Fe^{II}(N–N–N)_2]Br[Fe^{III}Br_4]$ were also obtained. The moment of $[Fe(N–N–N)_2](ClO_4)_2,3H_2O$ is temperature-dependent, ranging from 4·49 B.M. at 313 K to 2·23 B.M. at 83 K. The moment of the cation in $[Fe(N–N–N)_2]Br[FeBr_4]$ shows normal Curie–Weiss behaviour with but slight variation with temperature, varying from 5·23 to 4·85 B.M. over the temperature range 298—83 K.

COMPLEXES of iron(II), cobalt(II), and nickel(II) with α-di-imines have been extensively studied and form the subject of a recent review.[1] The α,α′,α″-tri-imine, 2,2′,2″-terpyridyl (I) was first reported in 1932 by Morgan and Burstall who also isolated the bis-ligand iron(II) complex as the bromide.[2] Since that time metal complexes of terpyridyl have received considerable attention.[3-9] These studies have led to the isolation of a number of five-co-ordinate mono-ligand complexes[4-7] and some bis-ligand complexes whose magnetic moments are temperature-dependent due to a thermal equilibrium, between spin-paired and spin-free configurations.[8,9]

The α,α′,α″-tri-imines, 2-(pyridylamino)-4-(2-pyridyl)-thiazole (II) and 2,4-bis(2-pyridyl)thiazole (III) have been shown to behave as planar tridentate ligands.[10,11] The mono-ligand complexes of these tridentates have been assigned five-co-ordinate structures, although in

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[1] L. F. Lindoy and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1967, **2**, 173.

[2] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1932, 20.

[3] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1937, 1649.

[4] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 1956, 594.

[5] J. S. Judge, W. M. Reiff, G. M. Intille, P. Ballway, and W. A. Baker, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1711.

[6] J. S. Judge and W. S. Baker, *Inorg. Chim. Acta*, 1967, **1**, 239, 245.

[7] W. M. Reiff, N. E. Erickson, and W. A. Baker, *Inorg. Chem.*, 1969, **8**, 2019.

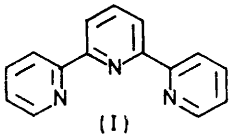
[8] J. S. Judge and W. A. Baker, *Inorg. Chim. Acta*, 1967, **1**, 68.

[9] C. M. Harris, T. N. Lockyer, R. L. Martin, H. R. H. Patil, E. Sinn, and I. M. Stewart, *Austral. J. Chem.*, 1969, **22**, 2105.

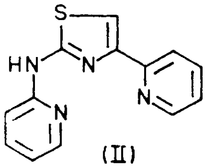
[10] H. A. Goodwin, *Austral. J. Chem.*, 1964, **17**, 1366.

[11] H. A. Goodwin and R. N. Sylva, *Austral. J. Chem.*, 1968, **21**, 1081, 2881.

some instances it is difficult to distinguish between the five-co-ordinate species $[MLX_2]$ and the salt-like species $[ML_2][MX_4]$.



(I)



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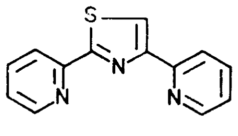
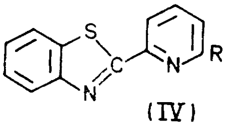


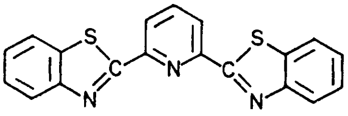
(III)

The α,α′-di-imines, 2-(2-pyridyl)benzothiazole (IV; R = H) and 2-(6-methyl-2-pyridyl)benzothiazole (IV; R = Me) act as bidentate ligands, co-ordinating through both nitrogen atoms.[12–14] The thiocyanato-complexes of cobalt(II) and copper(II) with the di-imine (IV; R = Me) are antiferromagnetic.[13] We now report the isolation and characterization of some metal complexes of the related α,α′,α″-tri-imine, 2,6-(dibenzothiazol-2-yl)pyridine (V) (N–N–N).

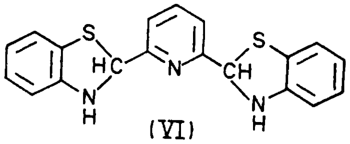
Preparation of the Tri-imine (V).—Pyridine-2,6-dicarbaldehyde, which was prepared by the method of Markovac *et al.*[15] for the conversion of methylpyridines into pyridinecarbaldehydes, was condensed with *o*-aminobenzenethiol to give the bis(benzothiazoline) (VI) which was not isolated but was oxidized *in situ* with iodine to give the tri-imine (V).



(IV)



(V)



(VI)

The tri-imine (V) differs from terpyridyl in that it has benzothiazolyl moieties in place of two of the pyridyl rings. Nevertheless it has the same tri-imine sequence and should behave like terpyridyl as a ligand, since it is fully aromatic with electron delocalization throughout the molecule. Like terpyridyl it must co-ordinate with all three nitrogen atoms in the one plane. However, heterocyclic nitrogen atoms in five-membered rings have poorer donor properties than those in pyridyl rings.[11] Furthermore, benzothiazole [16] (basic pK_a, 1·2) is a much weaker base than pyridine (pK_a, 5·2).[17] Consequently, the tri-imine (V) might be expected to form less-stable complexes than terpyridyl.

EXPERIMENTAL

2,6-(Dibenzothiazol-2-yl)pyridine.—2,6-Lutidine (36 g.) was treated with iodine (171 g.); the reaction mixture became quite warm. The iodine–lutidine complex, which solidified after the mixture had been cooled and the container had been scratched with a glass rod, was then added slowly, with stirring, to dimethyl sulphoxide (300 ml.) at 130°. The mixture was stirred and heated at 150° for 15 min., then cooled to 20°. *o*-Aminobenzenethiol (25 g.) was then added to the mixture and a vigorous reaction ensued. The mixture was cooled and the crystalline product was then filtered off, washed with alcohol, then with acetone, and recrystallized from chloroform to give pale yellow crystals of the *compound*; yield, 3 g. (9%), m.p. 273—275° (Found: C, 65·8; H, 3·3; N, 11·8; S, 18·6. $C_{19}H_{11}N_3S_2$ requires C, 66·1; H, 3·3; N, 12·2; S, 18·5%).

General Method of Preparation of Mono-Ligand Metal Complexes.—2,6-(Dibenzothiazol-2-yl)pyridine (0·345 g., 1 mmole) in hot chloroform (60 ml.) was added to a solution of the metal salt (1·2 mmole) in hot alcohol. The metal complex, which crystallized almost immediately, was filtered off, washed with hot chloroform, then with alcohol, followed by ether, and was then dried *in vacuo* over phosphorus pentoxide; yield, 70—90%.

Bis[*2,6-(dibenzothiazol-2-yl)pyridine*]*-iron*(II) *and -cobalt*(II) *Perchlorates and Fluoroborates.*—The metal perchlorate or fluoroborate (1 mmole) in hot alcohol (10 ml.) was added to a solution of 2,6-(dibenzothiazol-2-yl)pyridine (0·69 g., 2 mmole) in hot chloroform (120 ml.). The crystalline complex was deposited and was washed with chloroform, then with alcohol, followed by ether, and was then dried *in vacuo* over phosphorus pentoxide; yield, 60—85%.

Bis[*2,6-(dibenzothiazol-2-yl)pyridine*]*iron*(II) *Bromide Tetrabromoferrate*(III).—Anhydrous ferric bromide (0·296 g., 1 mmole) in hot alcohol (10 ml.) was added to a solution of 2,6-(dibenzothiazol-2-yl)pyridine (0·69 g., 2 mmole); the mixture was heated on a steam-bath for 5 min. and then cooled. The crystalline *complex* was then filtered off, and washed with chloroform and then with alcohol; it was dried *in vacuo* over phosphorus pentoxide; yield, 0·58 g. (95%).

Analyses.—Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne.

Magnetic Measurements.—The magnetic susceptibilities were measured by the Gouy method. Measurements other than at ambient temperature were made on a Newport variable-temperature Gouy balance.

Spectral Measurements.—The i.r. spectra were obtained from Nujol or halogenocarbon mulls on a Perkin-Elmer 337 spectrophotometer in the region 4000—400 cm^{-1} and on a Perkin-Elmer 521 spectrophotometer in the range 500—250 cm^{-1}.

The mass spectra were obtained on an MS-902 mass spectrometer.

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[12] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 1968, **22**, 119.

[13] P. S. K. Chia and S. E. Livingstone, *Inorg. Chim. Acta*, 1968, **2**, 427.

[14] P. S. K. Chia, L. F. Lindoy, and S. E. Livingstone, *Inorg. Chim. Acta*, 1968, **2**, 459.

[15] A. Markovac, C. L. Stevens, A. B. Ash, and B. E. Hackley, *J. Org. Chem.*, 1970, **35**, 841.

[16] A. Albert, R. Goldacre, and J. Phillip, *J. Chem. Soc.*, 1948, 2240.

[17] J. Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

X-Ray Diffraction Data.—The *X*-ray powder diffraction patterns were obtained with Cu-K_α radiation on a Phillips PW1010 generator with a Phillips camera of radius 57·3 mm.

RESULTS AND DISCUSSION

The condensation of *o*-aminobenzenethiol with pyridine-2-carbaldehyde yields not a Schiff base but a benzothiazoline, which can readily be oxidized to 2-(2-pyridyl)-benzothiazole (IV; R = H).[18] Consequently, it was expected that the product of the condensation of two equivalents of *o*-aminobenzenethiol with pyridine-2,6-dicarbaldehyde would be the bis(benzothiazoline) (VI), which ought to be readily oxidized to 2,6-(dibenzothiazol-2-yl)pyridine (V). Evidence for the formulation of the final product of the reaction (see Experimental section) as (V) is provided by its i.r. spectrum which shows no bands attributable to ν(N–H), δ(N–H), or ν(S–H).

TABLE 1

Mass spectral data for 2,6-(dibenzothiazol-2-yl)pyridine

m/e	Relative abundance	Reaction
345	100	$M^{\cdot +}$
319	16	Loss of $\cdot C{\equiv}N$
243	13	Loss of $\cdot C_6H_4$ from 319
237	13	Loss of $\cdot C_6H_4S\cdot$
211	33	Loss of $\underbracket{C_6H_4{\cdot}S{\cdot}\dot{C}{:}N}$
172½	23	$M^{\ddagger}$
134	6	$\underbracket{C_6H_4{\cdot}S{\cdot}\dot{C}{:}N}$
108	55	$\cdot C_6H_4S\cdot$

The mass spectrum of (V) shows a strong molecular-ion peak centred at *m/e* 345 (*M*, theor., 345). The other major peaks in the spectrum are listed in Table 1. The mass spectral data can be explained by the reactions given in the Scheme. These data supply strong confirmatory evidence for the formulation of the compound as (V).

The metal complexes which were obtained are listed in Table 2. The mono-ligand complexes are virtually insoluble in water and common organic solvents.

TABLE 2

Metal complexes of 2,6-(dibenzothiazol-2-yl)pyridine (N–N–N)

Compound	Colour	Magnetic moment at 298 K μ (B.M.)	Analyses % Calcd. Found C	H	N	S	M	Br
$Mn(N–N–N)Cl_2,\frac{1}{2}H_2O$	Yellow	5·92	47·5	2·5	8·75	13·6		
			47·4	2·3	8·7	13·5		
$Fe(N–N–N)Cl_2,\frac{1}{2}H_2O$	Dark green	5·38	47·5	2·5	8·8	13·3		
			47·1	2·2	8·6	12·9		
$Fe(N–N–N)Br_2$	Dark olive green	5·38	40·7	2·0	7·5	11·4	9·95	
			40·2	2·0	6·6	11·2	9·4	
$Fe(N–N–N)I_2$	Greenish black	5·31	34·8	1·7	6·4	9·8	9·5	
			34·9	1·5	6·2	9·3	9·0	
$Fe(N–N–N)(NCS)_2,\frac{1}{2}H_2O$	Greenish black	5·00	48·0	2·3	13·3	24·4	10·6	
			47·8	2·0	13·0	23·5	10·9	
$[Fe(N–N–N)_2](ClO_4)_2,3H_2O$	Reddish purple	4·40	45·6	2·8	8·4	12·8	5·9	
			45·5	3·1	8·1	12·4	5·1	
$[Fe(N–N–N)_2]Br[FeBr_4]$	Black	5·22 [a]	38·0	1·8	7·0	10·7	9·3	33·2
		6·02 [b]	38·4	2·1	6·7	10·3	9·4	32·9
$Co(N–N–N)Cl_2,\frac{1}{2}H_2O$	Buff	4·42	47·2	2·5	8·7	13·3	12·6	
			47·1	2·2	7·3	13·2	12·2	
$Co(N–N–N)Br_2$	Buff	4·51	40·45	2·0	7·45	11·4	10·4	
			40·0	2·0	7·2	11·2	10·5	
$Co(N–N–N)(NCS)_2$	Buff	4·54	48·5	2·1	13·45	24·6	11·3	
			48·5	2·2	13·3	23·7	11·3	
$Co(N–N–N)(NO_3)_2$	Light brown	4·42	43·2	2·1	13·25	12·1	11·2	
			43·1	2·3	12·9	11·9	11·2	
$[Co(N–N–N)_2](ClO_4)_2,5H_2O$	Orange	4·66	44·0	3·1	8·1	12·3	5·7	
			44·2	2·8	8·0	13·0	5·2	
$[Co(N–N–N)_2](BF_4)_2,4H_2O$	Orange	4·83	45·8	3·0	8·4	12·9	5·9	
			45·8	2·3	8·2	12·9	5·3	
$Ni(N–N–N)Cl_2$	Yellowish green	3·15	48·0	2·3	8·85	13·5	12·4	
			47·6	2·5	8·6	13·2	11·9	
$Ni(N–N–N)(NO_3)_2$	Green	3·15	43·2	2·1	13·3	12·1	11·1	
			42·8	2·3	12·1	12·0	11·1	

[a] For cation. [b] For anion.

The i.r. spectra of some of the mono-ligand complexes were measured down to 250 cm^{-1}. All the spectra display a well defined band of medium intensity in the range 369—365 cm^{-1}. This band, which is not present in the spectrum of the ligand, would seem to be associated with the metal–nitrogen stretching mode, and is tentatively assigned as ν(M–N). The frequencies are listed in Table 3. The frequency ν(M–N) can occur in the range 600—<200 cm^{-1}.[19] In pyridine complexes ν(M–N) usually occurs in the range 287—210 cm^{-1}.[20] However, more recently data based on isotopic shifts have shown that in the tris-ligand complexes $[M(N–N)_3]^{2+}$ (N–N = 1,10-phenanthroline and 2,2′-bipyridyl) ν(Fe–N) occurs in the

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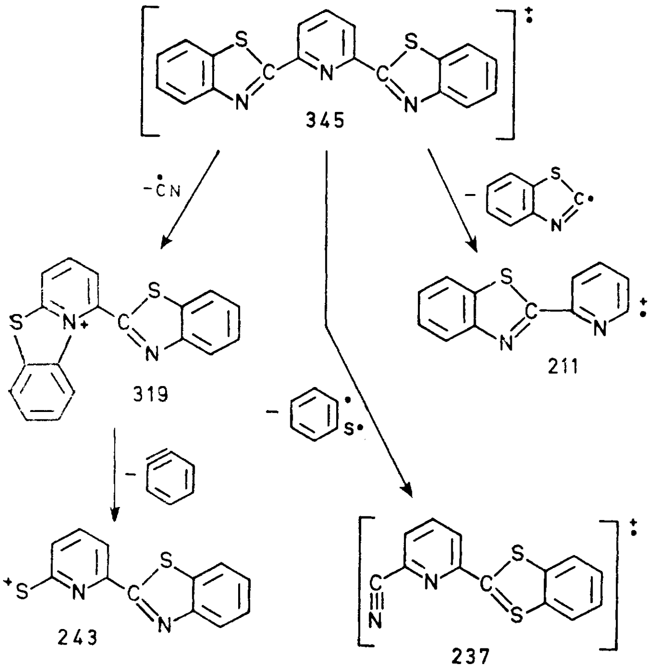
[18] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 1967, **1**, 365.

[19] D. M. Adams, 'Metal-Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 268.

[20] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.

range 386—359 cm^{-1} and ν(Ni–N) occurs at 300—240 cm^{-1}. In these complexes usually two bands were observed, although one was often weak.[21]



SCHEME

Reactions of 2,6-(dibenzothiazol-2-yl)pyridine in the mass spectrometer

I.r. bands attributable to ν(M–Cl) in the spectra of the chloro-complexes are also listed in Table 3. No bands appear in this region in the spectra of the bromo-complexes. Consequently, it seems reasonable to assume that these bands are associated with metal–chlorine vibrations, which occur in the range 400—200 cm^{-1}.[22] The occurrence of only one ν(M–Cl) band in the spectrum of the nickel complex, compared to three for the manganese and iron complexes and two for the cobalt complex, suggests that the nickel complex has a higher symmetry.

TABLE 3

Metal–nitrogen and metal–chlorine stretching frequencies

Compound	ν(M–N) (cm^{-1})	ν(M–Cl) (cm^{-1})
$Mn(N–N–N)Cl_2,\frac{1}{2}H_2O$	365	313, 295, 273
$Fe(N–N–N)Cl_2,\frac{1}{2}H_2O$	366	325, 294, 282
$Fe(N–N–N)Br_2$	368	
$Co(N–N–N)Cl_2,\frac{1}{2}H_2O$	366	320, 285
$Co(N–N–N)Br_2$	367	
$Ni(N–N–N)Cl_2$	369	271

The iron complexes $Fe(N–N–N)X_2$ (X = Cl, Br, I, NCS) are spin-free with moments within the range usually found for high-spin iron(II). The magnetic moment of the iodo-complex $Fe(N–N–N)I_2$ was measured over the temperature range 313—83 K; the moment is virtually independent of temperature, the Curie–Weiss constant θ having a value of −16°.

The bis-ligand complex $[Fe(N–N–N)_2](ClO_4)_2,3H_2O$ has a moment of 4·40 B.M. at room temperature. The moment is temperature-dependent and falls to 2·23 B.M. at 83 K (see Table 4). This deviation from Curie–Weiss behaviour is considered to be due to a thermal equilibrium between the spin-paired (t_{2g}^6) and spin-free ($t_{2g}^4e_g^2$) configurations of the iron(II) atom. The ligand-field strength of the tri-imine (V) must be very close to that required to make the A_{1g} (spin-paired) and $^5T_{2g}$ (spin-free) terms of the iron(II) atom in the $[FeN_6]$ chromophore nearly equi-energetic. It is noteworthy that the purple bis-terpyridyl complex $[Fe(terpy)_2]Br_2,H_2O$ is diamagnetic at room temperature.[23] This indicates that 2,2′,2″-terpyridyl has a greater tendency to cause spin-pairing of iron(II) than has the tri-imine (V).

TABLE 4

Magnetic data for $[Fe(N–N–N)_2](ClO_4)_2,3H_2O$

T (K)	$10^6\chi'_M$	$1/\chi'_M$	μ (B.M.)
313	7982	125·3	4·49
283	8011	124·8	4·21
243	7030	142·2	3·70
213	6433	155·4	3·32
173	5416	184·6	2·75
163	5387	185·6	2·66
143	5387	185·6	2·49
123	5331	180·8	2·34
103	6108	163·7	2·25
83	7434	134·5	2·23

If a solution of ferric bromide is added to the tri-imine (V) in alcohol, the black, crystalline complex $[Fe^{II}(N–N–N)_2]Br[Fe^{III}Br_4]$ is obtained. The magnetic moment displays Curie–Weiss behaviour, ranging from 5·62 B.M. per iron atom ($10^2\chi'_M$, 2·64) at 298 K to 5·29 B.M. ($10^2\chi'_M$, 8·68) at 83 K. The value of $10^2\chi'_M$ for $[NEt_4][Fe^{III}Br_4]$ is 1·50 (μ, 6·02 B.M.) at 298 K.[24] Subtraction of this value from 2·64 gives 1·14 for the molar susceptibility of the cation; this, in turn, gives a value of 5·23 B.M. for the moment of the cation in $[Fe(N–N–N)_2]Br[FeBr_4]$ at 298 K. Similarly a value of 4·85 B.M. was obtained for the moment of the cation at 83 K. Thus the moment varies only slightly with temperature in contrast to that of the same cation in $[Fe(N–N–N)_2](ClO_4)_2,3H_2O$. Accordingly, the magnetic behaviour of the bis-ligand cation $[Fe(N–N–N)_2]^{2+}$ is dependent on the nature of the anion.

The solid-state spectral data for the iron complexes are given in Table 5. The spectrum of $[Fe(N–N–N)_2](ClO_4)_2,3H_2O$ shows two weak broad bands at 9300 and 12,000 cm^{-1}. These two bands are considered to arise from the $^5E_g \leftarrow {}^5T_{2g}$ transition of high-spin octahedral iron(II). Splitting of this band into two components occurs in the spectra of most high-spin octahedral complexes of iron(II).[25] In the spectrum of

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[21] R. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Amer. Chem. Soc.*, 1970, **92**, 3335.

[22] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley–Interscience, New York, 1970, 2nd edn., p. 213; see also ref. 19, p. 26.

[23] R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341.

[24] A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, 1963, **2**, 817.

[25] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968, p. 249.

$[Fe(N{-}N{-}N)_2]Br[FeBr_4]$ the higher frequency band is obscured by the strong charge-transfer absorption of $[FeBr_4]^-$ above 12,000 cm^{-1}.

The spectra of the mono-ligand complexes $Fe(N{-}N{-}N)X_2$ (X = Cl, Br, I, NCS) differ from the spectra of the bis-ligand complexes in that they display one well resolved band of medium intensity in the region below 13,000 cm^{-1}. The bands above 15,000 cm^{-1} probably arise from charge-transfer transitions. These spectra resemble those of known five-co-ordinate complexes having the donor sets N_3Cl_2 [26] and of some other postulated five-co-ordinate iron(II) complexes having the donor sets N_2SX_2 (X = Cl, Br, NCS).[27] It seems likely that the complexes $Fe(N{-}N{-}N)X_2$ are five-co-ordinate. The i.r. spectrum of the thiocyanato complex displays a single ν(C≡N) absorption at 2055 cm^{-1}, indicative of terminal thiocyanato-groups. This suggests that the complex is monomeric and not polymeric octahedral with thiocyanato-bridges, since if this were the case, two ν(C≡N) frequencies would be expected.

TABLE 5

Solid-state reflectance spectra of iron complexes

Compound	Bands (cm^{-1})
$Fe(N{-}N{-}N)Cl_2$	8500, 15,500, 16,700sh
$Fe(N{-}N{-}N)Br_2$	8500, 16,800, 18,000sh
$Fe(N{-}N{-}N)I_2$	9800, 15,300, 17,000sh
$Fe(N{-}N{-}N)(NCS)_2$	9600, 17,000
$[Fe(N{-}N{-}N)_2](ClO_4)_2,3H_2O$	9300, 12,000sh, 17,600
$[Fe(N{-}N{-}N)_2]Br[FeBr_4]$	8500, *

* Strong absorption above 12,000 cm^{-1}.

With cobalt(II) the mono-ligand complexes $Co(N{-}N{-}N)X_2$ (X = Cl, Br, NCS, NO_3) and the bis-ligand complexes $[Co(N{-}N{-}N)_2]Y,nH_2O$ (Y = ClO_4, BF_4) were isolated. The bis-ligand perchlorate and fluoroborate have conductivities of 57 and 56 ohm^{-1} cm^2 $mole^{-1}$ in nitrobenzene at 25 °C The magnetic moments (see Table 2) of the bis-ligand complexes are within the range normally found for six-co-ordinate spin-free cobalt(II). The moments of the mono-ligand complexes are somewhat lower (4·42—4·54 B.M.). The moment of $Co(N{-}N{-}N)Br_2$ follows the Curie–Weiss law with a value of $-16°$ for θ. The moment of $Co(terpy)Br_2$ is also virtually independent of temperature, ranging from 4·9 at 293 to 4·7 B.M. at 77 K,[28] whereas the moments of complexes containing the cation $[Co(terpy)_2]^{2+}$ are anomalously low at room temperature and are temperature-dependent.[8,23,28,29]

The electronic spectral data for the cobalt complexes are listed in Table 6. The spectra of the bis-ligand complexes display two weak bands in the region 8500—12,000 cm^{-1} and a shoulder at *ca.* 20,000 cm^{-1}. These spectra are indicative of high-spin octahedral cobalt(II).[25] The spectrum of the nitrato-complex $Co(N{-}N{-}N)(NO_3)_2$ is similar, except that there is an additional absorption at 17,600 cm^{-1}. The spectrum suggests that this complex is six-co-ordinate. The spectra of the complexes $Co(N{-}N{-}N)X_2$ (X = Cl, Br, NCS) have more and better defined bands. These spectra are similar to those of five-co-ordinate cobalt(II) complexes.[26,27]

TABLE 6

Solid-state reflectance spectra of cobalt complexes

Compound	Bands (cm^{-1})
$[Co(N{-}N{-}N)_2](ClO_4)_2,5H_2O$	9000, 11,800, 20,000sh
$[Co(N{-}N{-}N)_2](BF_4)_2,4H_2O$	8600, 11,600, 19,600sh
$Co(N{-}N{-}N)(NO_3)_2$	8100, 13,000br, 17,600, 19,600sh
$Co(N{-}N{-}N)Cl_2$	4800, 9600, 15,600, 17,000, 19,400sh
$Co(N{-}N{-}N)Br_2$	4600, 5400, 9000, 11,000, 14,400, 16,800, 19,400sh
$Co(N{-}N{-}N)(NCS)_2$	4400, 5600, 8400, 11,800, 17,000, 19,600sh

The i.r. spectrum of the nitrato-complex shows well defined bands at 1476, 1420, 1293, 1278, and 1022 cm^{-1}. These bands are absent from the spectra of the complexes $Co(N{-}N{-}N)X_2$ (X = Cl, Br, NCS). The band at 1022 cm^{-1} is assigned as ν(N–O); this band occurs at *ca.* 1000 cm^{-1} in the spectra of all complexes containing co-ordinated nitrate.[30] The occurrence of four bands in the region 1500—1250 cm^{-1} suggests the presence of both bi- and uni-dentate nitrato-groups.[31,32] However, the low symmetry of this complex could give rise to splitting of the NO_2 stretching vibrations and the occurrence of four bands in this region is not conclusive evidence of the presence of both bidentate and unidentate nitrato-groups. Nevertheless the i.r. spectrum does give support to the postulate that this complex is six-co-ordinate. The i.r. spectrum of the thiocyanato-complex $Co(N{-}N{-}N)(NCS)_2$ displays one ν(C≡N) band at 2060 cm^{-1}, indicating the presence of terminal *N*-bonded thiocyanate and the absence of bridging thiocyanato-groups. This suggests that the compound is five-co-ordinate.

The only pure nickel complexes which were isolated were $Ni(N{-}N{-}N)X_2$ (X = Cl, NO_3). The electronic spectra of these complexes are typical of octahedral nickel(II).[25] The ν_1 transition $({}^3T_{2g} \leftarrow {}^3A_{2g})$ occurs at 9000 cm^{-1} for the chloro-complex and at 10,500 for the nitrato-complex, while the ν_2 transition $({}^3T_{1g} \leftarrow {}^3A_{2g})$ occurs at 14,000 cm^{-1} for the former and at 15,800 cm^{-1} for the latter. The ν_3 transition is obscured by strong ligand absorption above 24,000 cm^{-1}.

The i.r. spectrum of the nitrato-complex is similar to $Co(N{-}N{-}N)(NO_3)_2$ and displays five bands due to the nitrato-group at 1478, 1440, 1292, 1256, and 1011 cm^{-1}. This suggests the presence of both uni- and bi-dentate nitrato-groups. It is evident that the nickel complexes are six-co-ordinate. It seems likely that the chloro-

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complex is polymeric with chloro-bridges, whereas the nitrato-complex could be polymeric with one nitrato-bridge or monomeric with one unidentate and one bidentate nitrato-group.

The *X*-ray powder diffraction patterns of Fe(N–N–N)Cl_2 and Co(N–N–N)Cl_2 are similar but are different from those of Ni(N–N–N)Cl_2 and Mn(N–N–N)Cl_2. This is consistent with the spectral evidence that the iron and cobalt complexes are five-co-ordinate and the nickel complex is six-co-ordinate. The manganese complex may be either five- or six-co-ordinate.

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