Co-ordination Complexes of 2,2'-Bi-2-thiazoline and 2,2'-Bi-4,5-dihydrothiazine

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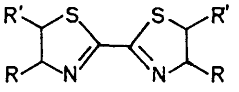
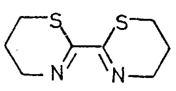
A number of complexes of 2,2'-bi-2-thiazoline, its 4,4'-dimethyl and 5,5'-dimethyl derivatives, and of 2,2'-bi-4,5-dihydrothiazine with Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Hg^{II}, and Mo^0 have been prepared. Structures of the complexes are deduced from infrared, electronic, ^1H n.m.r., and Mössbauer spectra, magnetic properties, and electrical conductances of solutions. The combined evidence afforded by these properties is consistent only with a co-ordination mode involving the α-di-imine group. Cyclic voltammetry of acetonitrile solutions of the tris-chelated iron(II) perchlorates shows two redox waves, one of which is ascribed to oxidation of the metal and the other to reduction of the co-ordinated ligand. The free-energy differences associated with these two couples correspond closely in magnitude to the energies of the metal-to-ligand charge-transfer bands occurring in the visible spectra. The properties of the complexes are compared with those of corresponding complexes of 2,2'-bipyridine and related ligands.

A RECENT report[1] of the ready synthesis of 2,2'-bi-2-thiazoline, (I), of its 4,4'- and 5,5'-dimethyl derivatives, (II) and (III), and of 2,2'-bi-4,5-dihydrothiazine, (IV), prompted us to examine their co-ordinating properties.

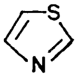


(I) R = R' = H (bt)
(II) R = Me, R' = H (btn)
(III) R = H, R' = Me (bts)

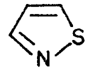


(IV) (btz)

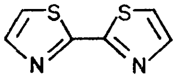
These molecules have the potential capability of forming five-membered ring chelates using (*a*) both nitrogen atoms, (*b*) both sulphur atoms, or (*c*) one nitrogen atom and one sulphur atom. In order to elucidate the co-ordination modes we have prepared and characterized complexes with a selection of (mainly) bivalent metal ions of differing class 'a'–class 'b' character. While it is known that the nitrogen atom is favoured in complexes of the (unidentate) conjugated ligands thiazole (V)[2] and isothiazole (VI),[3] it seemed possible that the presence in 2,2'-bi-2-thiazoline of two sulphur atoms suitably positioned for five-membered chelate-ring formation might render these the preferred donors to the softer metal-ion acceptors. This possibility was given added significance in view of the early report[4] that 2,2'-bithiazole, (VII), co-ordinates 'poorly' to iron(II) and that tris complexes could not be isolated. It was also of interest to compare the properties of the complexes with those of related ligands such as 2,2'-bipyridine. Like 2,2'-bipyridine, the thiazoline and thiazine ligands contain the α-di-imine chromophore but differ in that it is not part of an extended conjugated system.



(V)



(VI)



(VII)

RESULTS AND DISCUSSION

The complexes prepared are listed in Table 1 together with analytical and physical data pertaining to them. The choice of complex to be prepared was somewhat arbitrary but it includes complexes of metals of both 'hard' and 'soft' character. In most cases a ligand : metal ratio of not less than 3 : 1 was used. No exhaustive study of the products of reaction using other ligand : metal ratios was made so that complexes having other stoicheiometries may well be preparable. The complexes in Table 1 fall into five groups on the basis of stoicheiometry: (*i*) ML_3X_2 [M = Fe, Co, Ni, Cu, or Zn; X = ClO_4, BPh_4, $\frac{1}{2}(FeCl_4)$, or $\frac{1}{2}(ZnCl_4)$]; (*ii*) $Fe(btz)Cl_3$: (*iii*) $ML_2(NCS)_2$ (M = Co or Ni); (*iv*) MLX_2 (M = Zn or Hg; X = halide); and (*v*) $ML(CO)_4$.

The inference, based on stoicheiometry, that the complexes of group (*i*) are salts of the six-co-ordinate cations $[ML_3]^{2+}$ is supported by the electrical conductances of 10^{-3} mol dm^{-3} solutions in 1,2-dichloroethane or acetonitrile (Table 1) together with the good correspondence between solid-state and solution electronic spectra (Table 2). Moreover, i.r. spectra show that the X^- ions are unco-ordinated (see below). The same experimental criteria, where applicable, indicate that the $ML_2(NCS)_2$ and $MoL(CO)_4$ complexes have neutral six-co-ordinate structures while those in the MLX_2 group are neutral and four-co-ordinate although with partial ionic dissociation in a few cases. Attempts to prepare pure complexes of Fe^{III} were generally unsuccessful. In the case of bt, reduction to Fe^{II} usually occurred, while with btz the products of reaction appeared to be mixtures of two or more species. An exception is the complex of stoicheiometry $Fe(btz)Cl_3$ the properties of which are consistent with the formulation $[FeCl_2(btz)_2][FeCl_4]$ (see below).

Having established the probable co-ordination number of the metal in the different complexes, it remains to determine the mode of chelation. The evidence from

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[1] D. A. Tomalia and J. N. Paige, *J. Org. Chem.*, 1973, **38**, 3949.

[2] W. J. Eilbeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1967, 757.

[3] M. E. Peach and K. K. Ramaswamy, *Inorg. Chim. Acta*, 1971, **5**, 445; R. Rivest and A. Weisz, *Canad. J. Chem.*, 1971, **49**, 1750.

[4] H. Erlenmeyer and E. H. Schmid, *Helv. Chim. Acta*, 1939, **22**, 698; H. Erlenmeyer and H. Ueberwasser, *ibid.*, p. 932; 1940, **23**, 1268.

TABLE 1

Analytical, infrared, magnetic, and electrical conductance data for the complexes

		Analysis (%)									
		Found			Calc.					Λ [c]/S cm² mol⁻¹	
Complex	Colour	C	H	N	C	H	N	$\mu_{eff.}$ [a]/B.M.	$\tilde{\nu}$(C=N) [b]/cm⁻¹	$C_2H_4Cl_2$ [d]	MeCN [e]
$[Fe(bt)_3][ClO_4]_2$	Deep blue	28.2	3.3	10.7	28.0	3.1	10.9	0.98			337
$[Fe(bt)_3][FeCl_4]$	Deep blue	27.9	3.2	10.9	28.0	3.1	10.9	5.49 [f]			
$[Fe(bts)_3][ClO_4]_2$	Deep blue	33.4	4.4	9.7	33.7	4.2	9.8	0.85			250
$[Fe(btn)_3][ClO_4]_2$	Deep blue	33.6	4.2	10.0	33.7	4.2	9.8	0.94			297
$[Fe(btz)_3][ClO_4]_2$	Deep blue	33.9	4.0	9.6	33.7	4.2	9.8	0.98			327
$[Fe(btz)_3][BPh_4]_2$	Deep blue	66.7	6.0	6.4	66.8	5.9	6.5	0.70			207
$[Co(bt)_2(NCS)_2]$	Brick-red	32.4	3.2	16.1	32.2	3.1	16.1	4.98 [f]	1 582	[g]	[g]
$[Co(btz)_2(NCS)_2]$	Brick-red	37.7	4.3	14.8	37.5	4.2	14.6	4.91 [f]	1 572	[g]	[g]
$[Co(btz)_3][ClO_4]_2$	Peach	32.8	4.2	9.7	33.6	4.2	9.7	4.69 [f]	1 568		325
$[Co(btz)_3][BPh_4]_2$	Peach	66.8	6.0	6.5	66.6	5.9	6.5	5.03 [f]	1 560		225
$[Ni(bt)_3][ClO_4]_2$	Buff	27.9	3.3	11.0	27.9	3.1	10.9	3.19 [f]	1 567		328
$[Ni(bts)_3][ClO_4]_2$	Buff	33.1	3.8	9.4	33.6	4.2	9.8	2.98 [f]	1 568		273
$[Ni(btn)_3][ClO_4]_2$	Orange-red	33.9	4.0	10.3	33.6	4.2	9.8	3.08 [f]	1 568		297
$[Ni(btz)_3][ClO_4]_2$	Amber	34.3	4.3	9.9	33.6	4.2	9.8	3.02 [f]	1 570		308
$[Ni(bt)_2(NCS)_2]$	Olive green	32.4	3.1	16.3	32.2	3.1	16.1	3.11 [f]	1 582	[g]	[g]
$[Ni(btz))_2(NCS)_2]$	Olive green	37.6	4.1	14.4	37.6	4.2	14.6	3.13 [f]	1 572	[g]	[g]
$[Cu(btz)_3][ClO_4]_2$	Emerald green	33.5	4.0	9.5	33.4	4.2	9.7	1.82 [f]	1 568		334
$[Zn(bt)_3][ZnCl_4]$	White	26.8	3.1	10.5	26.9	3.0	10.5		1 580		
$[Zn(btz)_3][ClO_4]_2$	White	32.9	4.3	9.0	33.3	4.2	9.7		1 576		273
$[Zn(btz)_3][BPh_4]_2$	White	66.1	6.0	6.4	66.3	5.8	6.5		1 570		214
$[ZnBr_2(btz)]$	White	22.5	2.9	6.6	22.6	2.8	6.6		1 572	<0.5	15
$[HgBr_2(bt)]$	Cream	13.3	1.7	5.1	13.4	1.5	5.2		1 588	<0.5	7
$[HgI_2(bt)]$	Yellow	11.3	1.1	4.2	11.4	1.3	4.4		1 586	<0.5	8
$[HgCl_2(btz)]$	White	20.1	2.4	5.8	20.4	2.6	5.9		1 572		25
$[HgI_2(btz)]$	Yellow	14.8	2.0	4.1	14.7	1.9	4.3		1 580	<0.5	91
$[Mo(CO)_4(bt)]$	Purple	31.4	2.3	7.5	31.6	2.1	7.4			<0.5	
$[Mo(CO)_4(btz)]$	Purple	35.4	3.0	7.0	35.3	3.0	6.9			<0.5	

[a] The values quoted refer to 293 K. [b] For bt, bts, btn, and btz ν(C=N) occurs at 1 595, 1 593, and 1 614 cm⁻¹ respectively. [c] 10^{-3} mol dm⁻³ solutions. [d] Reported values for typical 1 : 1 electrolytes lie in the range 18—22 S cm² mol⁻¹. [e] Reported values for typical 2 : 1 electrolytes lie in the range 220—300 S cm² mol⁻¹ except for tetraphenylborates which have lower values (W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81). [f] Obeys the Curie–Weiss law in the range 90—300 K. [g] Insoluble.

TABLE 2

Electronic spectra of the complexes

Complex	State	Band maxima in 10^3 cm⁻¹ (ε/dm³ mol⁻¹ cm⁻¹)
$[Fe(bt)_3][ClO_4]_2$	Mull	18.0 (sh), 16.3
	MeCN	18.0 (sh), 16.8 (12 400)
	$MeNO_2$	17.8 (sh), 16.4, (8 800)
$[Fe(bt)_3][FeCl_4]$	Mull	29.8, 26.0 (sh), 17.4 (sh), 16.0
$[Fe(bts)_3][ClO_4]_2$	Mull	18.0 (sh), 16.3
	MeCN	17.8 (sh), 16.7 (8 500)
$[Fe(btn)_3][ClO_4]_2$	Mull	17.8 (sh), 16.2
	MeCN	23.5, 22.0 (sh), 20.0, 18.6 (sh)
	$MeNO_2$	18.1, 16.6 (decays with time, 3 000)
$[Fe(btz)_3][ClO_4]_2$	Mull	17.7 (sh), 16.0
	MeCN	18.0 (sh), 16.5 (10 100)
	$MeNO_2$	18.0 (sh), 16.4 (10 400)
$[Fe(btz)_3][BPh_4]_2$	Mull	17.8 (sh), 16.0
$[FeCl_2(btz)_2][FeCl_4]$	Mull	26.8 (sh), 23.6 (sh), 17.6 (sh), 15.8
$[Co(btz)_3][ClO_4]_2$	Mull	20.8 (sh), 11.2
	MeCN	21.2, 10.8 (6.5)
$[Co(btz)_3][BPh_4]_2$	Mull	20.4, 10.3
	MeCN	20.7 (sh), 10.4 (5.0)
$[Co(btz)_2(NCS)_2]$	Mull	19.3, 18.0 (sh), 9.4
$[Ni(bt)_3][ClO_4]_2$	Mull	18.4 (sh), 18.6
	MeCN	18.5 (sh), 18.6 (13)
$[Ni(bts)_3][ClO_4]_2$	Mull	18.5 (sh), 11.5
	MeCN	18.2, 11.5 (11)
$[Ni(btn)_3][ClO_4]_2$	Mull	20.2, 19.1, 17.5 (sh), 11.6, 10.8
$[Ni(btz)_3][ClO_4]$	Mull	11.2
	MeCN	11.6 (14)
$[Ni(btz)_2(NCS)_2]$	Mull	16.2, 10.3
$[Cu(btz)_3][ClO_4]_2$	Mull	15.9, 14.5 (sh), 8.6
	MeCN	16.0 (89), 13.3 (93), 10.0 (79)
$[Mo(CO)_4(bt)]$	Mull	18.5
	MeCN	18.6 (2 800)
$[Mo(CO)_4(btz)]$	Mull	18.4
	MeCN	18.5 (3 000)

magnetic properties and i.r., electronic, Mössbauer, and ^{1}H n.m.r. spectra is now considered.

Magnetic Properties.—The measured susceptibilities of the complexes of Fe^{II}, Co^{II}, and Ni^{II} provide support for the octahedral co-ordination of the metal ions and, in the case of the iron(II) complexes, further suggest that co-ordination is *via* the imino-nitrogen atoms. With the exception of the complex containing the $[FeCl_4]^{2-}$ counter ion, all the iron(II) complexes have magnetic moments not exceeding 1.1 B.M.,* consistent with spin-paired octahedral structures. The small residual paramagnetism is a generally observed property of such complexes and is attributable to temperature-independent paramagnetism (t.i.p.).[5] The observed moment of 5.49 B.M. at 293 K for $[Fe(bt)_3][FeCl_4]$ is as expected for a low-spin cation and high-spin anion.[6] Spin pairing in iron(II) complexes of α-di-imine ligands is well established,[7,8] and the observation that all the complexes described here have $S = 0$ ground states is strong evidence for co-ordination *via* the nitrogen atoms; thioethers exercise appreciably weaker ligand fields and spin pairing is not expected in these cases. It is interesting that the iron(II) complex of btn, which bears methyl substituents alpha to the nitrogen atoms,

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* 1 B.M. ≈ 9.27×10^{-24} A m².

[5] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev.*, 1968, **22**, 457.

[6] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

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

[8] E. König, *Co-ordination Chem. Rev.*, 1968, **3**, 471.

is also low spin. It might have been expected either that the complex should be high spin or that a tris-chelated complex would not be formed at all because of the steric effects of the methyl groups, as found for complexes of 2,9-dimethyl-1,10-phenanthroline and 6,6′-dimethyl-2,2′-bipyridine.[7] The reason for the smaller steric effect of btn compared with the latter may lie partly in the smaller ring size of btn but, more important, in the fact that the methyl substituents are not co-planar with the N=C–C=N group.

The single iron(III) complex prepared has a room-temperature magnetic moment of 5.76 B.M., calculated on the empirical formula of $Fe(btz)Cl_3$. Since the Mössbauer spectrum indicates the presence of two kinds of iron(III) sites, and since the i.r. spectrum showed a strong band at 385 cm^{-1} {due to ν(Fe–Cl) of $[FeCl_4]^-$}, it is concluded that the complex has the salt structure $[FeCl_2(btz)_2][FeCl_4]$. Assuming a moment of 5.9 B.M. for the anion, a value of 5.62 B.M. is calculated for the complex cation. This is measurably lower than the predicted value[6] of 5.9 B.M. The discrepancy may arise from a partial decomposition to a low-spin iron(II) species as found during the attempted preparation of some other iron(III) derivatives. In fact this complex changes to a deep blue colour on storage and on exposure to light.

The room-temperature moments of the cobalt(II) complexes fall at the lower end of the range usually associated with this ion in (weak) octahedral fields. In the case of the two $[Co(btz)_3]X_2$ salts the moments fall more steeply than is usual with decrease in temperature. Thus at 93 K the values are 4.42 ($X = ClO_4$) and 4.60 B.M. (BPh_4). There is no significant deviation from linearity in the Curie–Weiss plots in either case (θ *ca.* −30°). While the temperature dependence of the magnetic moment in these complexes may be associated merely with ground-state splittings due to spin–orbit coupling and low-symmetry components of the ligand field, it is worth noting that cobalt(II) complexes of several related α-di-imine ligands exhibit an anomalous temperature dependence of the magnetic moment which is due to a thermally controlled distribution between spin states.[9]

The magnetic moments of the nickel(II) complexes are typical of those expected for this ion in a six-co-ordinate field. The single copper(II) complex prepared is likewise magnetically normal. For neither of these metals do the magnetic data provide information on the mode of co-ordination.

Mössbauer Spectra of the Iron Complexes.—The spectra of the iron(II) complexes at 293 and 77 K consisted of a single quadrupole-split doublet in the case of $X = ClO_4$ and BPh_4 and of two quadrupole-split doublets in the case of $X = \frac{1}{2}(FeCl_4)$. The second (outer) doublet for the latter complex is assigned to the tetrahedral $[FeCl_4]^{2-}$ anion on the basis of the close comparison of the isomer shift (δ), the quadrupole splitting (ΔE_Q), and the temperature dependence of ΔE_Q with those of other complexes containing this complex anion.[10] The isomer shifts (0.2—0.4 mm s^{-1} relative to natural iron) and quadrupole splittings (0.3—0.5 mm s^{-1}) of the cations fall in the ranges expected for low-spin octahedral Fe^{II} (see Table 3). It may be significant that δ for $[Fe(btn)_3]^{2+}$ is slightly more positive than observed for the analogous bt and bts complexes. This is the predicted effect if btn exercises a smaller ligand field[11] (see Electronic Spectra).

TABLE 3

Mössbauer parameters for the iron complexes

Complex	T/K	δ [a,b]/ mm s^{-1}	ΔE_Q [b]/ mm s^{-1}
$[Fe(bt)_3][ClO_4]_2$	293	0.23	0.48
	77	0.31	0.50
$[Fe(bt)_3][FeCl_4]$	293	0.24	0.39
		0.95 [c]	1.82 [c]
	77	0.26	0.34
		0.99 [c]	2.86 [c]
$[Fe(bts)_3][ClO_4]_2$	293	0.24	0.39
	77	0.32	0.44
$[Fe(btn)_3][ClO_4]_2$	293	0.30	0.37
	77	0.36	0.40
$[Fe(btz)_3][ClO_4]_2$	293	0.24	0.39
	77	0.31	0.49
$[Fe(btz)_3][BPh_4]_2$	293	0.26	0.44
$[FeCl_2(btz)_2][FeCl_4]$	293	0.28 ± 0.05	0.44 ± 0.05
		0.17 ± 0.05 [c]	0.22 ± 0.05 [c]
	77	*d*	

[a] Relative to natural iron. [b] Estimated error ±0.02 mm s^{-1} except where otherwise indicated. [c] Refers to anion. [d] Poorly resolved.

The spectra obtained for the iron(III) complex $[FeCl_2(btz)_2][FeCl_4]$ are best interpreted in terms of two overlapping quadrupole-split doublets. The signal with the larger splitting is assigned to the octahedral cation while that with the smaller splitting is assigned to the tetrahedral $[FeCl_4]^-$ anion.[10]

Infrared Spectra.—All four ligands showed a strong ν(C=N) absorption at 1 590—1 620 cm^{-1} (Table 1) and strong bands in the 800—1 000 cm^{-1} region corresponding to skeletal vibrations of the heterocyclic ring. A weak-to-medium intensity band in the otherwise fairly clear 630—660 cm^{-1} region is tentatively assigned to the ν(C–S) stretch.

The spectra of the complexes differ from those of the free ligands in several major respects. Two distinct classes of spectra are clearly recognizable. In the first class [group (*i*)] fall all the high-spin and post-transition element complexes, while group (*ii*) contains the low-spin d^6 complexes of Fe^{II} and Mo^0. The close similarity, when allowance is made for variation in anionic ligand or counter ion, of the spectra within each group is strong evidence for a common co-ordination mode for all the complexes of the group.

Group (*i*) *complexes.* In these the strong ν(C=N) band was shifted to lower wavenumbers by 25—35 cm^{-1} without appreciable alteration in intensity. The pattern

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[9] R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Amer. Chem. Soc.*, 1961, **83**, 3732; J. S. Judge and W. A. Baker, *Inorg. Chim. Acta*, 1962, **1**, 68.

[10] N. N. Greenwood and T. C. Gibb, ‘ Mössbauer Spectroscopy,’ Chapman and Hall, London, 1971.

[11] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

of the 1 200—1 500 cm^{-1} region is similar to that of the free ligand but strong bands appeared at 1 000—1 250 cm^{-1} rather than at 800—1 000 cm^{-1}. A weak band at 640—680 cm^{-1} could be discerned in many of the spectra which may correspond to ν(C–S) of the co-ordinated ligand. It was difficult to identify this band in all cases because of its low intensity; however, there is no evidence of any systematic shift on complex formation as is observed for ν(C=N). Thus, the inference to be drawn from the internal-ligand spectra is that co-ordination is probably *via* the nitrogen atoms.

Examination of the spectra of the perchlorate complexes in the 200—400 cm^{-1} region revealed a medium-intensity band at 210—270 cm^{-1}. We feel confident that this is a metal–ligand stretching vibration and not an internal-ligand mode. No absorption was observed in this region in the free ligands nor in the mercury(II) complexes which are otherwise very similar. Nor was it observed in the spectra of the group (*ii*) complexes (see below). Table 4 compares the positions of these bands with the positions of the metal–ligand stretching modes of several corresponding 2,2′-bipyridine complexes.[12] It can be seen that there is a close similarity in the frequency of the absorption band in corresponding complexes of the two classes of ligand, the band consistently falling at slightly lower values in the case of the present complexes. This is taken as further evidence for nitrogen co-ordination.

TABLE 4

Comparison of metal–ligand stretching frequencies in some complexes of 2,2′-bi-2-thiazoline and 2,2′-bi-4,5-dihydrothiazine with those of analogous complexes of 2,2′-bipyridine

Complex	$\bar{\nu}$/cm^{-1}	Complex	$\bar{\nu}$/cm^{-1}
$[Co(btz)_3][ClO_4]_2$	253ms	$[Co(bipy)_3][ClO_4]_2$	266s, 228w
$[Ni(bt)_3][ClO_4]_2$	270ms	$[Ni(bipy)_3][ClO_4]_2$	278s, 260w
$[Ni(bts)_3][ClO_4]_2$	264ms		
$[Ni(btn)_3][ClO_4]_2$	259ms		
$[Ni(btz)_3][ClO_4]_2$	270ms		
$[Cu(btz)_3][ClO_4]_2$	267ms, br	$[Cu(bipy)_3][ClO_4]_2$	286s, 272w
$[Zn(btz)_3][ClO_4]_2$	211ms	$[Zn(bipy)_3][ClO_4]_2$	235s, 186w

s = Strong, ms = medium strong, br = broad, w = weak.

The i.r. spectra confirm conclusions reached earlier that the $[ClO_4]^-$ anions are not co-ordinated, there being no splitting of the ν_3 or ν_4 modes at *ca.* 1 090 and *ca.* 620 cm^{-1}, respectively. A strong band at 275 cm^{-1} in the spectrum of $[Zn(bt)_3][ZnCl_4]$ is attributed to ν(Zn–Cl) of the tetrahedral $[ZnCl_4]^{2-}$ anion. In the thiocyanato-complexes the position, intensity, and breadth of the ν(C=N) vibration suggest N-co-ordination of NCS. This band is split by *ca.* 13 cm^{-1}, suggesting a mutually *cis* arrangement of the NCS groups. It was not possible to identify the ν(C=S) vibration because of overlapping weak ligand absorption, but it is clear that it does not occur in the relatively transparent 700 cm^{-1} region expected for S-bonded NCS. Bands at *ca.* 470 cm^{-1} in these complexes are probably the NCS bending modes.

Group (*ii*) *complexes.* The most striking difference from the spectra of the group (*i*) complexes is the absence of any band of significant intensity in the ν(C=N) region. The absence of this vibration in the i.r. is an often noted feature of low-spin iron(II) α-di-imine chelates. It has been explained[13] on the basis that metal–ligand π-electron interaction in the five-membered chelate ring greatly alters the vibration frequency and intensity of the C=N group. In iron(II) complexes of pyridine-2-carbaldehyde azine a new band appears, at 85 cm^{-1} lower than in the free ligand, which has been assigned to the co-ordinated ν(C=N) vibration. In the present complexes the only new bands of appreciable intensity are 200 cm^{-1} lower in wavenumber. This seems large for a co-ordination shift. Also no bands occurred in the 200—300 cm^{-1} region, where we observed metal–ligand stretching modes for complexes of group (*i*), although in the bt complexes new weak bands at 350—450 cm^{-1} were observed.

The results of a normal-co-ordinate analysis by Nakamoto[14] on the low-spin tris-chelated complex of Fe^{II} with glyoxalbis(methylimine) show that there is strong coupling between modes in the chelate ring. In cases such as this the group-frequency approach is meaningless and characteristic C=N or metal–ligand modes cannot be identified.

Whatever the assignment of particular bands, the i.r. spectra of complexes in group (*ii*) provide clear evidence for strong perturbation of bonding in the α-di-imine moiety, and therefore for chelation of the metal by this group.

A strong band at 286 cm^{-1} in the spectrum $[Fe(bt)_3][FeCl_4]$ is assigned to ν(Fe–Cl) of $[FeCl_4]^{2-}$. Four ν(C=O) vibrations were seen in the 1 850—2 020 cm^{-1} region of the spectra of the molybdenum(0) complexes consistent with the *cis*-octahedral structure expected for them.

Electronic Spectra.—Spectra of solids (as Nujol mulls) and of solutions in acetonitrile and/or nitromethane were recorded in the range 5 000—30 000 cm^{-1} (see Table 2). Except where otherwise stated below, there was fair agreement between spectra in the two phases indicating that no major stereochemical rearrangement or decomposition occurs on dissolution.

The spectra of the iron(II) complexes showed little variation with change in ligand. All consisted of an intense visible band having a maximum at *ca.* 16 500 cm^{-1} and a shoulder on the high-energy side at *ca.* 18 000 cm^{-1}. Intense absorption in the visible region of the spectrum is once again a characteristic feature of low-spin octahedral iron(II) complexes of α-di-imine ligands.[7] Its occurrence in the present complexes is therefore further evidence for co-ordination of the ligands *via* the nitrogen atoms, for this metal at least.

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[12] Y. Saito, J. Takemoto, B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, 1972, **11**, 2003; W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1063.

[13] W. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 4834.

[14] K. Nakamoto, 'Advances in the Chemistry of Co-ordination Compounds,' ed. S. Kirschner, Macmillan, New York, 1961, p. 437.

The origin of the strong visible band is generally attributed to a charge transfer of metal t_{2g} electrons to vacant antibonding p_π orbitals of the chelate ring.[7,8,13] The energy of the charge-transfer band is appreciably lower than in most other complexes of this class {for example, in $[Fe(bipy)_3]^{2+}$ it occurs at 19 000 cm^{-1}}, an observation consistent with a high degree of involvement of the metal *d* electrons in the five-membered chelate ring, as inferred earlier from the i.r. spectra. The complex ion $[Fe(btn)_3]^{2+}$ decomposes in solution, possibly as a result of the steric effect of the methyl groups in the 4,4′-positions.

It is probable that the intense visible band occurring in the molybdenum(0) complexes has a similar charge-transfer origin. Again, the energies of these bands are lower than in corresponding 2,2′-bipyridine complexes.[15] It is noteworthy, also, that the dithioether complex $[Mo(CO)_4(MeSCH_2CH_2SMe)]$ does not absorb below *ca.* 24 000 cm^{-1}.[16]

TABLE 5

^{1}H N.m.r. data for the ligands and complexes

		τ				
	Solvent	H^4,$H^{4'}$	Me_4	H^5,$H^{5'}$	Me_5	H^6, $H^{6'}$
bt	$CDCl_3$	5.55 (t) [a]		6.63 (t) [a]		
	$(CD_3)_2CO$	5.59 (t) [a]		6.63 (t) [a]		
btn	$CDCl_3$	5.22 (st) [f,b]	8.57 (d) [b]	6.5—7.0 (m) [f,g]		
bts	$CDCl_3$	5.6 (m)		6.0 (m)	8.62 (d) [c]	
btz	$CDCl_3$	6.14 (t) [d]		8.12 (p) [d,e]		7.01 (t) [e]
$[Mo(CO)_4(bt)]$	$CDCl_3$	5.37 [a]		6.26 [a]		
$[Zn(bt)_3][ZnCl_4]$	$(CD_3)_2CO$	5.57 [a]		6.52 [a]		
$[HgI_2(bt)]$		5.32 [a]		6.57 [a]		
$[Mo(CO)_4(btz)]$	$CDCl_3$	5.82 [d]		7.95 [d,e]		6.81 [e]
$[ZnBr_2(btz)]$	$CDCl_3$	5.96 [d]		7.87 [d,e]		6.76 [e]
$[HgI_2(btz)]$	$CDCl_3$	6.04 [d]		7.95 [d,e]		6.86 [e]

[a] $J(H^4H^5)$ 8.2 Hz. [b] $J(H^5Me)$ 6.5 Hz. [c] $J(H^4Me)$ 7.0 Hz. [d] $J(H^4H^5)$ 5.4 Hz. [e] $J(H^5H^6)$ 6.0 Hz. [f] $J(H^4H^5)$ (*cis* and *trans*) 7.5, 8.5 Hz. [g] $J(H^5H^{5'})$ 10.7 Hz.

Strong absorption in the near ultraviolet due to the co-ordinated ligand partly obscures or overlaps the *d–d* spectra of the complexes of Co^{II} and Ni^{II}. The spectra of the cobalt(II) complexes consist of an asymmetric maximum at *ca.* 21 000 cm^{-1} and another weaker maximum at *ca.* 10 500 cm^{-1} in the case of the tris-(ligand) complexes; in the thiocyanate the two main absorptions are at somewhat lower energies. This is the expected pattern for high-spin Co^{II} in an octahedral field of nitrogen donors.[17] Neglecting distortions from octahedral symmetry, the lower-energy maximum is assigned to the $^4T_{1g}\rightarrow{}^4T_{2g}$ transition and the higher-energy band to the (overlapping) transitions $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and $^4T_{1g}\rightarrow{}^4A_{2g}$.

Because of overlapping ligand or metal–ligand charge-transfer absorption in the near-u.v. only two of the three spin-allowed bands predicted for octahedral Ni^{II} could be identified in the spectra of the complexes of bt, bts, and btn, and only one in the spectra of the btz complexes with the exception of the thiocyanate. In the absence of distortion the energy of the longest-wavelength band, $^3A_{2g}\rightarrow{}^3T_{2g}$, is a direct measure of 10 *Dq*, the ligand-field-splitting parameter. It can be seen from Table 2 that *Dq* is *ca.* 1 160 cm^{-1} in the case of the tris-chelated complexes of bt, bts, and btz, and measurably lower in the case of the btn complex for which there is also some evidence of splitting of both *d–d* bands. These field strengths may be compared with those of other octahedral amine complexes of Ni^{II}. They are lower than *Dq* of $[Ni(bipy)_3]^{2+}$ (1 265 cm^{-1}) but comparable with *Dq* of, for example, $[Ni(en)_3]^{2+}$ (1 150 cm^{-1}) (en = 1,2-diaminoethane).[17] Where six neutral saturated sulphur atoms constitute the octahedral field *Dq* is significantly lower. In $[Ni(2,5\text{-dithiahexane})_3][ClO_4]_2$, for example, *Dq* is 1 060 cm^{-1}.[18] The complex $Ni(btz)_2(NCS)_2$, which is isomorphous with the corresponding cobalt(II) complex, probably has a *cis* configuration as noted above. The *Dq* value of this complex case is again somewhat lower. No splitting of either of the two observed *d–d* bands was detected.

The spectrum of $[Ni(btn)_3][ClO_4]_2$ differs from the others in two respects. First, both *d–d* bands were slightly split and the centre of gravity of the lower-energy band was *ca.* 600 cm^{-1} lower in energy. This is taken as further evidence for co-ordination *via* the α-di-imine group in these complexes, the presence in btn of methyl substituents adjacent to the donor nitrogens serving to weaken the metal–ligand interaction and to distort the complex.

The complex $[Cu(btz)_3][ClO_4]_2$ is isomorphous with the cobalt(II) analogue. In octahedral symmetry a single *d–d* transition in the low-energy visible or near-i.r. regions is expected,[17] *viz.* $^2T_{2g}\rightarrow{}^2E_g$. The occurrence of three bands of comparable intensity in this region of the spectrum of $[Cu(btz)_3][ClO_4]_2$ indicates some distortion from this symmetry, but without further information such as polarized crystal spectra it is not possible to define the nature of this distortion.

^{1}H *N.M.R. Spectra*.—Data for the free ligands bt, bts, and btz were reported by Tomalia and Paige.[1] However, the data are incomplete and the assignments of the methylene protons are in error.* Our assignments,

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* These appear to be based on a misinterpretation of the work of M. A. Weinberger and R. Greenhaigh, *Canad. J. Chem.*, 1963, **41**, 1038.

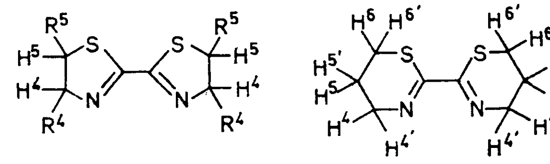
[15] M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.

[16] J. A. Connors and G. A. Hudson, *J.C.S. Dalton*, 1975, 1025.

[17] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, 1968.

[18] R. L. Carlin and E. Weissburger, *Inorg. Chem.*, 1964, **3**, 611.

with chemical shifts and coupling constants, are given in Table 5 according to the numbering schemes given below.



bt ($R^4 = R^5 = H$)
btn ($R^4 = Me$, $R^5 = H$)
bts ($R^5 = Me$, $R^4 = H$)

btz

Only a few of the diamagnetic complexes were sufficiently soluble in appropriate solvents for satisfactory spectra to be obtained. In all cases the spectra of the complexes are very similar to those of the uncomplexed ligands. Protons in one half of the ligand are still equivalent to the corresponding protons in the other half. This would seem to rule out the co-ordination mode which uses one nitrogen and one sulphur atom. All the proton resonances showed small downfield shifts on co-ordination without change in coupling constants. It might have been expected, as commonly observed, that protons bound to carbons adjacent to the donor atoms would suffer the greater chemical shift. No such correlation is apparent in this work. For example, the H^4 and $H^{4'}$ protons are most shifted in $[Mo(CO)_4(btz)]$ whereas in $[Mo(CO)_4(bt)]$ the largest shift is shown by H^5 and $H^{5'}$. Yet for both complexes other evidence indicates co-ordination *via* the nitrogen atoms. We conclude that ^1H n.m.r. co-ordination shifts are not diagnostic of the co-ordination mode of these ligands.

TABLE 6

Cyclic voltammetry data for the $[Fe(ligand)_3][ClO_4]_2$ complexes in acetonitrile (10^{-3} mol dm^{-3}). Supporting electrolyte, 0.1 mol dm^{-3} $[NEt_4][ClO_4]$; potentials in V *versus* s.c.e.; sweep rate 0.03—0.2 V s^{-1}

	First redox step			Second redox step			Third redox step			Fourth redox step		
Complex	$E_{\mathrm{P_c}}{}^1$	$E_{\mathrm{P_a}}{}^1$	$E^{\ominus 1}$	$E_{\mathrm{P_c}}{}^2$	$E_{\mathrm{P_a}}{}^2$	$E^{\ominus 2}$	$E_{\mathrm{P_c}}{}^3$	$E_{\mathrm{P_a}}{}^3$	$E^{\ominus 3}$	$E_{\mathrm{P_c}}{}^4$	$E_{\mathrm{P_z}}{}^4$	$E^{\ominus 4}$
$[Fe(bt)_3][ClO_4]_2$	1.03	1.11	1.07	−0.96	−0.88	−0.92						
$[Fe(bts)_3][ClO_4]_2$	1.02	1.10	1.06	−0.96	−0.88	−0.92						
$[Fe(btz)_3][ClO_4]_2$	0.72	0.79	0.755	−1.28	−1.19	−1.235	−1.43	−1.37	−1.40			
$[Fe(bipy)_3][ClO_4]_2$	0.09	1.05	1.02	−1.43	−1.37	−1.40	−1.60	−1.54	−1.57	−1.90	−1.80	−1.85

Electrochemical Measurements.—Cyclic voltammetry was carried out on dilute solutions (10^{-3} mol dm^{-3}) of the perchlorate salts of the $[FeL_3]^{2+}$ complex ions (L = bt, bts, and btz) in acetonitrile using 10^{-1} mol dm^{-3} $[NEt_4][ClO_4]$ as supporting electrolyte. Measurements were also made on solutions of $[Fe(bipy)_3][ClO_4]_2$. Two redox waves were observed in the range +1.2 to −1.4 V for the bt and bts complexes, three for the btz complexes, and three for the btz complex. The 2,2'-bipyridine complex showed four redox waves between +1.2 and −2.0 V. Values of $E_{\mathrm{P_c}} - E_{\mathrm{P_a}}$ were close to the theoretical value of 0.058 V for a reversible one-electron-transfer process in all cases (see Table 6). However, the reduced species formed during the more negative redox process in the case of the bt and bts complexes have short lifetimes. The most positive wave (denoted the 'first redox process' in Table 6) in each case is ascribed to a redox process occurring at the metal, *viz.* Fe^{III}–Fe^{II}. It can be seen that the potentials $E^{\ominus 1}$ *versus* the standard calomel electrode (s.c.e.) for this process are appreciably different for the bt and bts complexes on the one hand and the btz complex on the other, the former having values very close to that of the bipy complex. Thus, the five-membered-ring ligands bt and bts stabilize the lower oxidation state (II) of the metal more effectively than the six-membered-ring analogue. No doubt this is the reason for our failure to isolate iron(III) complexes of bt.

The three redox processes ($E^{\ominus 2}$, $E^{\ominus 3}$, and $E^{\ominus 4}$) occurring between −1.3 and −1.9 V in acetonitrile solutions of $[Fe(bipy)_3][ClO_4]_2$ and related complexes have previously been assigned [19] to reductions at the metal to give, successively, complexes of Fe^I, Fe^0, and Fe^{-I}. Other workers [20] have suggested that the added electrons are not localized on the metal but are transferred to ligand π orbitals. In our view this is the more reasonable interpretation. An argument against the localization of added charge on the metal is that the energy separations between the couples are very small. Similarly, we propose that in the second redox process ($E^{\ominus 2}$) in the bt and bts complexes the added electron resides principally on a ligand with formation of a (unstable) radical anion; in the case of $[Fe(btz)_3]^{2+}$ two of the three ligands are successfully reduced.

Support for the above views come from a consideration of the low-energy charge-transfer absorption occurring in the visible spectrum. This was assigned as due to a transfer of a metal $d_\pi(t_{2g})$ electron to the lowest-unoccupied p_π antibonding orbital of the α-di-imine moiety, *i.e.* a metal-oxidation–ligand-reduction process. If our assignments are correct we might therefore except some correlation in the energies of the electrochemical and spectral processes. The function $F(E^{\ominus 1} - E^{\ominus 2})$ is the free energy associated with removal of an electron from Fe^{II} in the complex and addition of an electron to to the co-ordinated ligand. It is compared in Table 7 with the energy of the charge transfer derived from the visible spectra for the four complexes. The correspondence is remarkably good in all cases, bearing in

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[19] N. Tanaka and Y. Sato, *Electrochim. Acta*, 1968, **13**, 335; S. Musumeci, E. Rizzarelli, S. Sammartano, and R. P. Bonomo, *J. Inorg. Nuclear Chem.*, 1974, **36**, 853.

[20] I. Hanazaki and S. Nagakura, *Bull. Chem. Soc. Japan*, 1971, **44**, 2312.

mind that the two energies refer to different, although similar, processes. They are the same, in that in both cases an electron is transferred from a molecular orbital localized mainly on the metal of the ground-state iron(II) complex. They differ in that in the electrochemical process the reduced species is a ground-state anionic complex of Fe^{II} whereas, in the spectral process, the reduced species is an excited state of a neutral complex having appreciable iron(III) character. Moreover, the electrochemical process represents a free-energy change, whereas the charge-transfer absorption band refers to a change in internal energy. The closeness of the numerical agreement may, therefore, be coincidental and we attach significance principally to the observation that the two energies change together in the same sense as the nature of the ligand is altered. It is interesting that although $E^{\ominus 1}$ and $E^{\ominus 2}$ are appreciably different for the bt and btz complexes, the difference $E^{\ominus 1} - E^{\ominus 2}$ is the same in the two cases. The reason for the larger $E^{\ominus 1} - E^{\ominus 2}$ value for the bipy case is presumably due to the occurrence of cross-conjugation effects which serve to reduce the contribution of the α-di-imine p_π electrons to the chelate ring.

TABLE 7

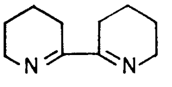
Comparison of the energies of the charge-transfer bands with those of the metal–ligand redox process

	Energy/kJ mol^{-1}	
Complex	Charge transfer *	$F(E^{\ominus 1} - E^{\ominus 2})$
$[Fe(bt)_3][ClO_4]_2$	201	192
$[Fe(bts)_3][ClO_4]_2$	200	191
$[Fe(btz)_3][ClO_4]_2$	197	192
$[Fe(bipy)_3][ClO_4]_2$	227	233

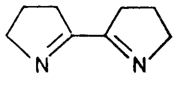
* Values for MeCN solutions.

Conclusions.—Considered collectively the evidence of the physical properties of the complexes leaves little doubt that in every case examined the ligands bond to metal *via* the nitrogen donors, demonstrating the superiority of the co-ordinating properties of the α-di-imine group even in those cases where the metal ion is known to have an affinity for sulphur.

Some comparisons of the properties of the complexes with those of analogous bipy complexes have already been noted. We have seen (*i*) that both 2,2′-bi-2-thiazoline and 2,2′-di-4,5-dihydrothiazine exercise smaller ligands fields, (*ii*) that their co-ordinating ability is less affected by methyl substitution at the carbon atoms adjacent to the nitrogen donors, and (*iii*) that the metal-oxidation charge-transfer band occurs at appreciably lower energies. The latter effect is considered to be a consequence of the occurrence in bipy complexes of cross conjugation which serves to reduce the involvement of the α-di-imine p_π electrons in chelate-ring delocalization. An implication of this is that the metal is more easily oxidized and/or the co-ordinated ligand more easily reduced in the case of the bt and btz complexes, a prediction borne out by the electrochemical results. Other ligands more closely related to bt and btz are 2,2′-bi-3,4,5,6-tetrahydropyridine, (VIII), and 2,2′-bipyrroline, (IX).[21] These have been little studied; no magnetic properties of the iron(II) complexes have been reported but they show intense absorption at 18 500 cm^{-1} and are presumably low spin. The apparent failure[4] of 2,2′-bithiazole, (VII), to form analogous complexes with Fe^{II} seems anomalous.



(VIII)



(IX)

EXPERIMENTAL

The crude ligands were synthesized according to the methods described by Tomalia and Paige.[1] Purification was by Soxhlet extraction with hexane and subsequent recrystallization from hexane, carbon tetrachloride, or acetone. Yields were generally lower than reported in the above work. The material reported as bt by Tomalia and Paige was clearly impure as judged by its solubility properties.

Complexes were prepared by the addition of an ethanolic solution of the appropriate metal salt to a slightly greater than stoicheiometric quantity of the ligand in warm ethanol with brisk stirring. In most cases the product complex precipitated immediately or after standing for a few minutes. In others (complexes of Zn and Hg) solvent was slowly removed until crystals appeared. Yields were generally in excess of 50%. The iron(II) and molybdenum(0) complexes were prepared under oxygen-free conditions. The molybdenum(0) complexes were prepared by refluxing $[Mo(CO)_6]$ and ligand in 1 : 1 proportions in dry toluene for 2 h. The purple colour of the complex developed quickly on heating and purple crystals separated on cooling.

Physical Measurements.—Infrared spectra were recorded in the range 200—4 000 cm^{-1} as Nujol mulls and as KBr or CsBr pellets using Perkin-Elmer 457 grating or Grubb–Parsons DM4 spectrometers. A Unicam SP 700 spectrophotometer was used in measurements of the electronic spectra. The spectra of the solids are transmittance spectra of Nujol mulls. A conductivity cell of cell constant 0.0368, constructed from bright platinum electrodes, was used in conjunction with a resistance–capacitance bridge in measurements of electrical conductivity. Magnetic measurements were made by the Gouy method using a Newport Instruments variable-temperature magnetic balance. Mössbauer spectra were recorded at 293 ± 3 and 77 K with a ^{57}Co in Pd source using a Harwell constant-acceleration spectrometer. The equipment was calibrated with an iron-foil standard at 293 K. Absorber thicknesses were not more than 50 mg cm^{-2}. Isomer shifts and quadrupole splittings were determined by visual inspection.

Electrochemical experiments were carried out under a dry N_2 atmosphere. All electrode potentials were measured with respect to an aqueous s.c.e. (1.0 mol dm^{-3} $Na[NO_3]$) salt bridge containing the electrolysis solution so as to avoid precipitation of $K[ClO_4]$ at liquid junctions. The latter were made of short 3-mm diameter plugs of porous Vycor glass attached to the glassware by polytetrafluoroethylene (p.t.f.e.) tubes. The cell for cyclic voltammetry had an s.c.e. reference, a platinum-wire anode, and an

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[21] P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163.

appropriate cathode and was controlled by an operational amplifier-potentiostat unit built in this Department. The potential waveform cam from a Hewlitt–Packard 3310A function generator and current–voltage curves were recorded as a Bryant 2600 series XY recorder. The bright platinum cathode was allowed to reach equilibrium at the starting potential, then the result from a single triangular voltage sweep was recorded. The cathode was formed from a platinum sphere made by melting platinum wire (0.30-mm diameter) in a hydrogen–oxygen flame and supported in soda glass.

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