Chromium(II) Chemistry. Part 11.[1] Further Investigations of Complexes of 2,2′-Bipyridyl and 1,10-Phenanthroline

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Various mono- and bis-(amine)halides and thiocyanates of Cr^{II} have been prepared. The complexes $[Cr(bipy)X_2]$ and $[Cr(phen)X_2]$ (bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, X = Cl or Br) are high spin but with considerable antiferromagnetic interaction due to halide bridging in octahedral structures, while $[Cr(bipy)_2X_2]$ (X = I or SCN) and $[Cr(phen)_2]$ are low spin. Infrared data show that the thiocyanato-complexes have a *cis-N*-bonded configuration.

OCTAHEDRAL complexes of transition elements in oxidation states having the electronic configurations d^4, d^5, d^6, or d^7 can be high or low spin according to the strength of the ligand field. Additionally, certain octahedral complexes with the last three *d* configurations, in which the ligand-field stabilization energy is close to the spin-pairing energy, have been found to exhibit spin equilibria, but this type of behaviour[2] does not seem to have been reported for the d^4 situation, *e.g.* in chromium(II) complexes. Most known chromium(II)

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[1] Part 10, L. F. Larkworthy and J. M. Tabatabai, *J.C.S. Dalton*, 1976, 814.

[2] R. L. Martin and A. H. White, *Transition Metal Chem.*, 1968, **4**, 113.

complexes are high spin [for $t_{2g}^3e_g^1$ configuration, μ(spin only) 4.90 B.M.*] but $K_4[Cr(CN)_6]$,[3] the tris(amine) complexes[4] of 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen), $Cr(terpy)_2I_2\cdot H_2O$[5] (terpy = 2,2′:6′,2″-terpyridyl), and the recently reported diarsine complexes[6] are low spin [for t_{2g}^4 configuration, μ(spin only) 2.83 B.M.]. From stability-constant data[7] it has been suggested that a change of spin state occurs in aqueous solution on the addition of a second bipy molecule to the chromium(II) ion, presumably when the species $[Cr(bipy)_2(OH_2)_2]^{2+}$ is formed. There are also scattered reports that certain solid bis(2,2′-bipyridyl)chromium(II) complexes are low spin, *i.e.* $[Cr(bipy)_2Cl_2]$, $[Cr(bipy)_2(O_2CMe)_2]$,[8] $[Cr(bipy)_2(OH_2)_2][ClO_4]_2$, and $[Cr(bipy)_2Br_2]\cdot H_2O$.[9] This paper reports investigations of new mono(amine) and bis(amine) complexes (Table 1) of Cr^{II} synthesised in attempts, albeit unsuccessful, to produce the crossover situation with the d^4 configuration.

RESULTS AND DISCUSSION

Mono(amine) Complexes.—At room temperature the magnetic moments of the complexes $[Cr(amine)X_2]$ (Table 1) are somewhat below the value (4.8—4.9 B.M.) usually found for high-spin chromium(II) complexes and decrease considerably with decreasing temperature. Similar antiferromagnetic behaviour has been reported for other mono(amine)chromium(II) complexes[10] which are believed to be halide-bridged and six-co-ordinate. The Curie–Weiss plots † show slight curvature so the θ values (Table 1) are approximate. It is therefore assumed that the mono(amine) complexes of bipy and phen have similar polymeric structures, although co-ordination of water in the phen complexes is possible.

The reflectance spectra of the complexes are as commonly found for chromium(II) ions in distorted-octahedral environments, the broad bands (Table 2) near 14 000 cm^{-1} being assigned to superimposed $^5B_1\rightarrow{}^5B_2,{}^5E$ transitions, and the shoulders near 11 000 cm^{-1} to the $^5B_1\rightarrow{}^5A_1$ transition. The mono(amine) complexes dissolve in water, and this breaks up the polymeric structures as can be seen from the difference between the reflectance and aqueous-solution spectra (Table 2). The spectra show that, by disproportionation, both mono- and tris-(bipy) complexes form the corresponding bis complexes, whereas mono(phen) complexes form the corresponding tris complexes [equations (1)—(3)]. The complexes $[Fe(phen)_2X_2]$ also disproportionate in water and methanol.[11] The ratios

$$2[Cr(bipy)X_2] \longrightarrow [Cr(bipy)_2X_2] + CrX_2 \qquad (1)$$

$$[Cr(bipy)_3]X_2 \longrightarrow [Cr(bipy)_2X_2] + bipy \qquad (2)$$

$$3[Cr(phen)X_2] \longrightarrow [Cr(phen)_3]X_2 + 2CrX_2 \qquad (3)$$

of the molar absorption coefficients agree reasonably with the stoicheiometry of the reactions, but are only approximate because the spectra change with time even in a nitrogen atmosphere, and some spectra were recorded in ethanol and others in water. Absorption due to CrX_2 ($\varepsilon_{max.}$ 5 dm^3 mol^{-1} cm^{-1} at 14 000 cm^{-1})[12] or bipy in the 8 000—30 000 cm^{-1} region is negligible in comparison with the absorption of the amine complexes.

Bis(amine) Complexes.—The complexes $[Cr(bipy)_2(NCS)_2]$ and $[Cr(phen)_2(NCS)_2]$ are the first aminethiocyanates of Cr^{II} to be isolated, and the latter is the only known bis(phenanthroline) complex. Since iodide and *S*-bonded thiocyanate are among the ligands with the weakest fields, bis(amine) complexes of Cr^{II} with these anions were synthesized as they might have provided the first examples of spin equilibria in the d^4 case. However, the iodo-complex is low spin down to liquid-nitrogen temperature (Table 1), as are the thiocyanato-complexes, but the i.r. absorptions of the thiocyanato-groups (Experimental section) show[13] that they are *N*-bonded so that spin pairing is not surprising. The *N*-bonding suggests that low-spin Cr^{II} can be classified among the class A metals.

The ground term of low-spin Cr^{II} is $^3T_{1g}$ (t_{2g}^4 configuration), and incomplete quenching of the orbital contribution is expected to lead to magnetic moments greater than the spin-only value. This was found for the bis(amine) complexes, but the moment of the iodo- is considerably larger than the moments of the thiocyanato-complexes. The magnetic behaviour of the $^3T_{1g}$ term, under the influence of an axial ligand-field component and spin–orbit coupling, has been given by Figgis *et al.*[14] These perturbations, and also increasing covalency of the metal–ligand bonds as estimated by the orbital-reduction factor k, can lead to lower and less temperature-dependent magnetic moments than would otherwise be expected, but the observed magnetic behaviour of the thiocyanates can be replicated only by assuming very low values of k. This casts doubt on the applicability of the model and suggests the presence of a ligand-field component of lower symmetry as might be

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* Throughout this paper 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 Oe ≈ 79.58 A m^{-1}.

† The magnetic data are to be found in Supplementary Publication No. SUP 22128 (3 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[3] R. W. Asmussen, 'Magnetokemiske Undersögelser over Uorganiske Komplexs forbindelser,' Gjellerups Forlag, Copenhagen, 1944, p. 123.

[4] A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin, and E. G. Terezakis, *J. Chem. Soc. (A)*, 1966, 511; E. G. Terezakis and R. L. Carlin, *Inorg. Chem.*, 1967, **6**, 2125.

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[10] A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc. (A)*, 1970, 1840; L. F. Larkworthy, K. C. Patel, and J. K. Trigg, *ibid.*, 1971, 2766.

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[13] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

[14] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. (A)*, 1966, 1411.

expected with *cis* complexes (see below). Mathematical treatments of such situations do not appear to be available.

The splitting of the ν(CN) band shows that *cis*-isothiocyanato-groups are present. This splitting is of the same magnitude as that found for *cis*-$[Fe(phen)_2(NCS)_2]$ and the frequencies lie between those of the high-spin isomers of this complex. This implies[15] that the extent of back bonding from metal to amine is less than in the low-spin iron(II) complex, which is to be expected because of the fewer *d* electrons in the low-spin chromium(II) complexes.

TABLE 1

Magnetic data and elemental analyses

Complex	$\mu_{eff.}$ [a]/B.M. 295	$\mu_{eff.}$ [a]/B.M. 90 K	θ [a]/K	10^6 × Diamagnetic correction (cm^3 mol^{-1})	Analyses (%) [b] C	H	N	Cr	Halide
$[Cr(bipy)Cl_2]$	4.19	3.60	*ca.* 45	−152	43.3	3.3	10.0	18.8	25.7
					(43.0)	(2.9)	(10.0)	(18.65)	(25.4)
$[Cr(bipy)Br_2]$	4.37	3.75	*ca.* 45	−174	32.8	2.4	7.6	14.3	43.3
					(32.6)	(2.2)	(7.6)	(14.1)	(43.4)
$[Cr(bipy)_2I_2]$	3.35	3.32	2	−311	39.2	3.3	9.2	8.5	42.8
					(38.9)	(2.6)	(9.1)	(8.4)	(41.1)
$[Cr(bipy)_2(NCS)_2]$	2.91	2.86	2	−272	54.5	3.3	17.6	10.6	
					(55.0)	(3.3)	(17.5)	(10.8)	
$[Cr(phen)Cl_2]\cdot H_2O$	4.57	3.90	*ca.* 60	−188	45.7	3.2	8.6	16.2	22.0
					(44.9)	(3.1)	(8.7)	(16.2)	(22.1)
$[Cr(phen)Br_2]\cdot H_2O$	4.54	3.90	*ca.* 60	−210	35.4	2.6	6.8	12.8	39.8
					(35.15)	(2.5)	(6.8)	(12.7)	(39.0)
$[Cr(phen)_2(NCS)_2]\cdot H_2O$	3.07	3.06	0	−331	58.0	3.6	15.6	9.55	
					(57.1)	(3.3)	(15.4)	(9.5)	

[a] Calculated from $\mu_{eff.} = 2.828\ (\chi_A T)^{\frac{1}{2}}$ and the Curie–Weiss law, $\chi_A^{-1} \propto (T + \theta)$. [b] Calculated values are given in parentheses.

TABLE 2

Reflectance and solution electronic spectra

Complex	Absorption bands (cm^{-1})							
$[Cr(bipy)_3]Br_2$ [a,b]	30 800m	23 600m	17 000m	15 000m	11 000 (sh)	9 400 (sh)	8 400s	8 000 (sh)
	28 000 (sh)	21 400	17 700	14 200	12 600 (sh)	9 800 (sh)	8 400	
	(*ca.* 5 300)	(3 600)	(4 400)	(2 000)	(*ca.* 1 900)	(*ca.* 2 800)	(7 200)	
$[Cr(bipy)_2I_2]$	28 000 (sh)	21 400s	17 000s	13 500 (sh)	12 400s	9 200 (sh)	8 500vs	7 500 (sh)
	28 000 (sh)	21 400	17 700	14 200	13 000 (sh)	9 600 (sh)	8 500	
	(*ca.* 4 000)	(2 500)	(2 800)	(1 300)	(*ca.* 1 300)	(*ca.* 2 000)	(5 200)	
$[Cr(bipy)Cl_2]$	24 000vb, s		18 000 (sh)	14 000 (sh)	11 400 (sh)			
	28 000 (sh)	21 400	17 700	14 200	12 600 (sh)	9 800 (sh)	8 400	
	(*ca.* 1 800)	(1 300)	(1 400)	(710)	(*ca.* 640)	(*ca.* 1 000)	(2 700)	
$[Cr(bipy)Br_2]$	22 600vb, s		18 400 (sh)	14 000	11 000 (sh)			
	28 000 (sh)	21 400	17 700	14 200	12 600 (sh)	9 800 (sh)	8 400	
	(*ca.* 1 500)	(1 100)	(1 200)	(600)	(*ca.* 530)	(*ca.* 840)	(2 200)	
$[Cr(bipy)_2(NCS)_2]$		19 600s	16 400s		13 400s		8 400vs	
$[Cr(phen)_3]I_2\cdot 2H_2O$ [b]	28 400 (sh)	24 800 (sh)	20 800s	18 200 (sh)		11 500s	9 400 (sh)	8 500s
	28 600 (sh)	25 600 (sh)	21 000	18 400 (sh)	15 600 (sh)	12 000	9 800 (sh)	8 600
	(*ca.* 5 600)	(*ca.* 4 700)	(2 900)	(*ca.* 450)	(*ca.* 710)	(3 500)	(*ca.* 3 700)	(*ca.* 10 000)
$[Cr(phen)Cl_2]\cdot H_2O$	28 000 (sh)	23 000s	21 800 (sh)	18 000 (sh)	14 000 (sh)	11 000 (sh)		
	28 800 (sh)	25 500	20 800	18 400 (sh)	15 000 (sh)	12 000	9 800 (sh)	(8 500)
	(*ca.* 1 600)	(1 400)	(1 000)	(*ca.* 150)	(*ca.* 380)	(1 100)	(*ca.* 1 200)	(3 600)
$[Cr(phen)Br_2]\cdot H_2O$	28 000 (sh)	23 400 (sh)	21 800	18 400 (sh)	14 000	11 000 (sh)		
	29 000 (sh)	25 600	20 800	18 400 (sh)	15 600 (sh)	12 000	9 800 (sh)	8 500
	(*ca.* 1 500)	(1 300)	(880)	(*ca.* 140)	(*ca.* 220)	(1 000)	(1 200)	(3 200)
$[Cr(phen)_2(NCS)_2]\cdot H_2O$	24 000s	19 100m				11 500s		8 300s

[a] Reflectance bands are given in the first row for each complex. Figures in parentheses are molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) referring to solution bands immediately above. Spectra of aqueous mono(amine) complexes or ethanolic solutions. The spectra of the mono(amine) complexes are quoted only as evidence for disproportionation. [b] Similar spectra were obtained for other tris(amine) halides.

The complexity of the i.r. spectra of $[Cr(bipy)_2I_2]$, $[Cr(bipy)_2(NCS)_2]$, and $[Cr(phen)_2(NCS)_2]$ in the 700—800 cm^{-1} region is further confirmation[16] of a *cis* configuration. The spectra of the bis(amine) complexes are also very similar to those of $[Cr(bipy)_3]X_2$ and $[Cr(phen)_3]X_2$.

The spectrum of $[Cr(bipy)_3]Br_2$ in ethanol is very similar to that obtained by König and Herzog[17] for a methanolic solution of the same complex. However, our results suggest that disproportionation had occurred in methanol too. Also, the similarity between the spectrum of $[Cr(bipy)_3]Br_2$ in methanol solution and the reflectance spectrum[17] of $[Cr(bipy)_3][ClO_4]_2$ suggests that the perchlorate is a bis(2,2′-bipyridyl) complex,

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[15] E. König and K. Madeja, *Spectrochim. Acta*, 1967, **A23**, 45.

[16] W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1964, **26**, 15; E. König and K. Madeja, *Inorg. Chem.*, 1967, **6**, 48.

[17] E. König and S. Herzog, *J. Inorg. Nuclear Chem.*, 1970, **32**, 585.

perhaps $[Cr(bipy)_2(OH_2)_2][ClO_4]_2$.[9] Only a figure depicting its reflectance spectrum was given, but it appears very different from our spectra of tris(2,2′-bipyridyl) complexes. Bands up to 32 000 cm^{-1} in the electronic spectra of apparently tris(2,2′-bipyridyl)chromium(II) complexes have been designated [17] as charge transfer in character, and those above 32 000 cm^{-1} as internal-ligand transitions.

EXPERIMENTAL

The halogeno-complexes were generally prepared by the addition of an ethanolic solution of a calculated amount of the ligand to an ethanolic solution of the hydrated chromium(II) halide [12] under nitrogen. The solids were filtered off, washed with ethanol, and dried under continuous pumping. The complex $[Cr(bipy)_2I_2]$ was isolated from acetone.

In order to prepare the thiocyanato-complexes, an aqueous solution containing chromium(II) bromide hexahydrate and ammonium thiocyanate in 1 : 2 molar ratio was added very slowly and with constant shaking to a solution of a stoicheiometric amount of the amine in aqueous ethanol. The brown product was filtered off, washed with water, and dried. Addition of metal ion to amine was necessary since reverse addition gave products of uncertain composition, probably through formation of mono(amine) complexes.

Infrared bands (cm^{-1}) arising from the thiocyanate groups have been assigned as follows: $[Cr(bipy)_2(NCS)_2]$, ν(CN) at 2 082s and 2 070s; 2δ(NCS) 985w; ν(CS) 838vw and 826vw; δ(NCS) 487s; ν(M–NCS) 362m and 347s; and $[Cr(phen)_2(NCS)_2]\cdot H_2O$, ν(CN) at 2 078s and 2 062s; 2δ(NCS) 965vw; ν(CS) 836m; δ(NCS) 494m and 474w; ν(M–NCS) 363s,br and 335m.

Chromium and halide were determined as before.[4] The metal in the thiocyanates was determined by direct combustion to Cr_2O_3. Magnetic measurements were carried out by the Gouy method from room to liquid-nitrogen temperature on samples sealed *in vacuo* in Pyrex tubes. The apparatus, calibrated with nickel(II) chloride solution, was that described earlier,[18] or a model obtained from Newport Instruments, Newport Pagnell, Bucks. Electronic spectra were recorded on a Unicam SP 700C spectrophotometer provided with a SP 735 diffuse-reflectance attachment and a lithium fluoride reference. No dilution of the solids was necessary. The samples were sealed in cells under nitrogen.

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[18] A. Earnshaw, *Lab. Practice*, 1961, **10**, 294.