

931. *The Co-ordination Number of Transition-metal Ions. Part II.¹ Configuration Equilibria in Solutions of Complexes of Cobalt(II) with Quinoline and Isoquinoline.*

By H. C. A. KING, E. KÖRÖS, and S. M. NELSON.

The magnetic and electronic spectral properties of the compounds CoL_nX_2 (L = quinoline or isoquinoline, X = halide or pseudohalide ion) are described. All of the solid bisamine complexes ($n = 2$) have tetrahedral structures. Only when L = isoquinoline could the octahedral tetrakisamine complexes ($n = 4$) be prepared. The bisquinoline complexes show partial disproportionation into ionic species in nitromethane and chloroform solution, and, in the presence of excess of quinoline, show no tendency to form the octahedral adduct. These effects are discussed in terms of intramolecular steric hindrance. In contrast, the tetrahedral bisisoquinoline molecules in chloroform solution in the presence of excess of isoquinoline exist in equilibrium with octahedral tetrakisquinoline molecules. Thermodynamic functions for these equilibria are interpreted in terms of a variable degree of $d_{\pi}-p_{\pi}$ bonding between metal and amine in the octahedral adduct, the extent of π -overlap being determined by the nature of X. In these complexes isoquinoline appears to be a better π -acceptor than pyridine.

IN PART I¹ we described the results of a thermodynamic investigation of the configurational equilibrium (1) in chloroform, where L = py = pyridine and X = halide or pseudohalide



ion. It was found that the nature of the anionic ligand X has a striking effect on the position of equilibrium. Thus, when X = halide or NCO^- the tendency of the tetrahedral complex to co-ordinate two free pyridine molecules to become octahedral is small whereas with NCS^- as ligand the octahedral complex is relatively much preferred. Calorimetric determinations of the heat of reaction indicated that entropy effects were, for the most part, dominant, and to explain the results it was suggested that there is a measure of dative π -bonding, $\text{Co} \rightarrow \text{py}$, in the metal-pyridine bond and that the extent of this back-co-ordination is controlled by the nature of X. Steric effects were considered less important than electronic effects except when pyridine was replaced by its 2-methyl derivative. That the degree of π -overlap between metal and heterocyclic amine seemed to depend so markedly on the character of the anionic ligand partner was interesting, and in order to test the generality of the conclusions we have now examined complexes of quinoline and isoquinoline. Quinoline complexes seemed worthy of study also because there seems to be doubt whether quinoline exercises a steric effect in the formation of six co-ordinate complexes MQ_4X_2 (M = bivalent metal ion, Q = quinoline).²⁻⁴

RESULTS

Two types of solid complex were examined, those with two molecules of heterocyclic amine per metal atom, CoL_2X_2 , and those with four, CoL_4X_2 . Only with L = isoquinoline, however, could the latter type be prepared. The preparation of several of the complexes has been described;⁵ only one, $\text{CoQ}_2(\text{NCSe})_2$, has been structurally characterised.⁶ Magnetic moments (17–19^o) and reflectance spectra for all the solid complexes are in Tables 1 and 2.

¹ Part I, King, Körös, and Nelson, *J.*, 1963, 5449.

² Goodgame and Goodgame, *J.*, 1963, 207.

³ Grossmann and Hunseler, *Z. anorg. Chem.*, 1905, **46**, 386.

⁴ Reitzenstein, *Lieb. Ann.*, 1894, **282**, 277.

⁵ See Gmelin's *Handbuch der anorg. Chemie*, 1930, **58B**.

⁶ Cotton, Goodgame, Goodgame, and Haas, *Inorg. Chem.*, 1962, **1**, 565.

TABLE 1.

Complex	Colour	Magnetic moment (B.M.)	Complex	Colour	Magnetic moment (B.M.)
CoQ ₂ Cl ₂	Blue	4.42	Co(IQ) ₂ I ₂	Dark green	4.50
CoQ ₂ Br ₂	Blue	4.43	Co(IQ) ₂ (NCS) ₂	Blue	4.61
CoQ ₂ I ₂	Dark green	4.75	Co(IQ) ₄ Cl ₂	Pink	4.95
CoQ ₂ (NCO) ₂	Blue	4.47	Co(IQ) ₄ Br ₂	Pink	5.20
CoQ ₂ (NCS) ₂	Blue	4.25	Co(IQ) ₄ I ₂	Tan	5.40
CoQ ₂ (NCSe) ₂	Dark green	4.39 ⁶	Co(IQ) ₄ (NCO) ₂	Pink	4.94
Co(IQ) ₂ Cl ₂	Blue	4.54	Co(IQ) ₄ (NCS) ₂	Pink	4.98
Co(IQ) ₂ Br ₂	Blue	4.45	Co(IQ) ₄ (NCSe) ₂	Tan	5.02

TABLE 2.

Complex	State	$\lambda_{\max.}$ (m μ)	Complex	State	$\lambda_{\max.}$ (m μ)
CoQ ₂ Cl ₂	Solid	~585sh, 620, ~665sh	Co(IQ) ₂ I ₂	Solid	~610sh, 660, 690
	CHCl ₃ soln.	~583sh, 615, 635, ~660sh		CHCl ₃ soln.	~620sh, 660, 690
CH ₃ NO ₂ soln.	582, ~618sh, 635	CH ₃ NO ₂ soln.		~620sh, 658, 688, ~735sh (the 735 m μ band disappears on addition of excess IQ)	
CoQ ₂ Br ₂	Solid	600, ~620sh, 660	Co(IQ) ₂ (NCO) ₂	Solid	555, 585, 630, 655
	CHCl ₃ soln.	~600sh, ~635sh, 655		CHCl ₃ soln.	553, 593, 630, ~650sh
CH ₃ NO ₂ soln.	598, ~630sh, 648	CHCl ₃ soln.		~565sh, 600, 627	
CoQ ₂ I ₂	Solid	620, 660, 690	CH ₃ NO ₂ soln.	~575sh, 610	
	CHCl ₃ soln.	~630sh, 660, 690	Co(IQ) ₄ Cl ₂	Solid	505, 530, ~560sh
CH ₃ NO ₂ soln.	~625sh, 662, 694, 737 (the 737 m μ band disappears on addition of excess Q)	CHCl ₃ -IQ soln.*		507, 531, ~555sh	
CoQ ₂ (NCO) ₂	Solid	550, 585, 630, 655	Co(IQ) ₄ Br ₂	Solid	520, ~540sh, ~570sh
	CHCl ₃ soln.	550, 580, 630, ~655sh		CHCl ₃ -IQ soln.*	525, ~545sh, ~570sh
CoQ ₂ (NCS) ₂	Solid	~570sh, 600, ~630sh	Co(IQ) ₄ I ₂	Solid	510-600 (poorly resolved)
	CHCl ₃ soln.	~570sh, ~610sh, 622		CHCl ₃ -IQ soln.*	515, 545, ~570sh
CoQ ₂ (NCSe) ₂	CH ₃ NO ₂ soln.	~575sh, ~610sh, 620	Co(IQ) ₄ (NCO) ₂	Solid	470, ~508sh, ~555sh
	Solid	560, 590, 610		CHCl ₃ -IQ soln.*	470, ~505sh, 550
Co(IQ) ₂ Cl ₂	CHCl ₃ soln.	~565sh, 615	Co(IQ) ₄ (NCS) ₂	Solid	480, 500, ~550sh
	Solid	580, 610, 650		CHCl ₃ -IQ soln.*	~480sh, 498, ~545sh
Co(IQ) ₂ Br ₂	CHCl ₃ soln.	582, 610, 630	Co(IQ) ₄ (NCSe) ₂	Solid	480-550 (poorly resolved)
	CH ₃ NO ₂ soln.	582, 615, ~640sh		CHCl ₃ -IQ soln.*	490, ~540sh
Co(IQ) ₂ I ₂	Solid	600, 630, 650	* 9 : 1 w/w CHCl ₃ -IQ soln.		
	CHCl ₃ soln.	600, ~630sh, 650			
	CH ₃ NO ₂	598, ~630sh, 650			

For the Co(IQ)₄X₂ series (IQ = isoquinoline) the magnetic moments all fall in the range 4.9—5.4 B.M. usually associated with spin-free six co-ordinate cobalt(II).⁷ The solid-state spectra all show weak absorption in the 460—560 m μ region, again characteristic of cobalt(II) in this environment.⁷ The differences in the positions of the spectral bands with change in the anionic ligand X are consistent with the positions of the X ions in the spectrochemical series. In no case could we isolate octahedral complexes containing quinoline in place of isoquinoline. This conflicts with the claim by Reitzenstein to have prepared CoQ₄Cl₂ by recrystallising anhydrous cobalt(II) chloride from quinoline.⁴

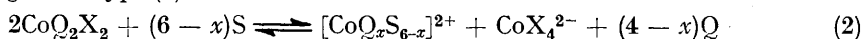
Tables 1 and 2 also include magnetic and spectral data for the solid bisamine complexes. For these the moments fall in the range 4.2—4.8 B.M. usually encountered for tetrahedrally co-ordinated cobalt(II).⁷ In agreement with this assignment the visible spectral bands at 570—700 m μ agree closely in position, profile, and intensity with those of related cobalt complexes of known tetrahedral constitution.⁸ The multicomponent nature of the visible band, which in *T_d* symmetry corresponds to the transition ⁴A₂ → ⁴T₁(P), arises presumably from spin-orbit coupling and is frequently observed in spectra of tetrahedral cobalt complexes.⁸ The variation of the position of the centre of gravity of the visible band with change in X leads to the following order of ligand field strength: I⁻ < Br⁻ < Cl⁻ <

⁷ Cotton and Wilkinson, "Advanced Inorganic Chemistry," Interscience Publ., Inc., New York, 1962, p. 723.

⁸ Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1777, and other Papers in same series.

$\text{NCO}^- < \text{NCS}^- < \text{NCSe}^-$. This is the order generally accepted for the halide and pseudo-halide ions in which the bonding to the metal is through the nitrogen atom.^{8,9} The effect of varying ligand field strength seems to be reflected also in the magnetic moments of the bisquinoline complexes. For example, the iodide, in which the average ligand field is weakest, has the highest moment (4.75 B.M.), whereas the thiocyanate, having a much greater ligand field, has a moment of only 4.25 B.M. Such a correlation is to be expected, at least if one assumes not too widely differing spin-orbit coupling constants.^{8,10} But with the isoquinoline series, the observed moments span only a very small range of values (0.15 B.M.) which is comparable with the experimental uncertainty (± 0.07 B.M.), so no correlation is evident here. Variations in compression forces have been suggested by Cotton and his co-workers¹⁰ to account for the variability in the magnetic moments of tetrahalogenocobalt(II) anions in crystals with different cations. A similar explanation might well apply here since the two series of complexes probably have widely different packing requirements in the crystal lattice owing to the differing symmetries of the two isomeric amine molecules about the metal-nitrogen bond. In any event all the bisamine complexes clearly have a basically tetrahedral configuration as was previously demonstrated for one of them, $\text{CoQ}_2(\text{NCSe})_2$.⁶

Complexes in Solution.—The bisamine complexes were examined spectrally in the visible range in both chloroform and nitromethane and also in chloroform containing up to 10% of the appropriate amine. Molar extinction coefficients (ϵ) for the spectra in solution without added amine are high ($\epsilon \sim 400\text{--}1000$) as expected for tetrahedral cobalt(II) complexes; Table 2 shows that there is close correspondence between the positions of the solid and solution spectral bands. This suggests that the complexes dissolve without extensive decomposition. However, a careful examination of the solution spectra indicated that the quinoline complexes partially decompose in solution, and more so in nitromethane than in chloroform. From the observations described below we believe the decomposition to be of the general type (2), where S = solvent.



In support of a measure of such disproportionation, all the quinoline complexes showed deviations from Beer's law in nitromethane solution, apparent molar extinction coefficients (ϵ) decreasing with decreasing concentration. Such deviations were much less evident in chloroform but were still serious for $\text{CoQ}_2(\text{NCS})_2$ and $\text{CoQ}_2(\text{NCSe})_2$. Successive additions of small amounts of quinoline to solutions of the quinoline complexes (in either solvent but particularly in nitromethane) increased the height of the tetrahedral absorption bands up to a point beyond which further additions produced no further effect. This is consistent with the view that free quinoline is a decomposition product and that it exists in equilibrium with the undissociated tetrahedral complex, as represented by reaction (2). In some cases, *e.g.*, CoQ_2Cl_2 , added amine also altered the profile of the absorption, as illustrated in Figs. 1 and 2. Curve A of Fig. 1 is the spectrum of $10^{-3}\text{M-CoQ}_2\text{Cl}_2$ in nitromethane without added quinoline; curve B is for the same solution containing 0.006 mole per litre of quinoline. In addition to an overall enhancement of the tetrahedral band on addition of quinoline, the absorption at $625\text{ m}\mu$, which on Curve A occurs only as a shoulder, becomes relatively more intense with respect to the peaks at 638 and $586\text{ m}\mu$, and the shoulder at $\sim 670\text{ m}\mu$. It is interesting to compare these spectral changes with the absorption spectrum of the CoCl_4^{2-} anion in the same solvent (Curve C).¹¹ This tetrahedral anion has absorption maxima at wavelengths (640 , 588 , and $675\text{ m}\mu$) very close to those at which the CoQ_2Cl_2 solution without added quinoline shows anomalously strong absorption. In fact, a curve essentially identical to spectrum A can be constructed from spectra B and C by weighting them in the ratio of $\sim 4:1$. It seems then, that CoQ_2Cl_2 partially decomposes into CoCl_4^{2-} and other species in nitromethane, as suggested above. In

⁹ Nelson, *Proc. Chem. Soc.*, 1961, 372.

¹⁰ Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

¹¹ Turco, Pecile, and Niccolini, *Proc. Chem. Soc.*, 1961, 213.

qualitative agreement with this we also found that the electrical conductance (Λ_M) of this same solution fell from a value of $\Lambda_M = 28$ mho at 20° , on successive additions of small amounts of quinoline, to a steady value of approximately 13.5 mho. Control experiments showed that the effect of added quinoline on nitromethane alone was to *increase* the conductance. This decrease in conductance of the CoQ_2Cl_2 solutions on addition of quinoline parallels closely the rise in apparent molar absorbance of the visible absorption band (Fig. 2). It is significant that even in the presence of up to about 10% quinoline

FIG. 1. Effect of added quinoline on the visible spectrum of 10^{-3}M - CoQ_2Cl_2 in nitromethane.

- (A) No added quinoline.
 (B) Containing 0.006 mole quinoline per litre.
 (C) CoCl_4^{2-} ($[\text{AsPh}_4]_2[\text{CoCl}_4]$; ref. 11).

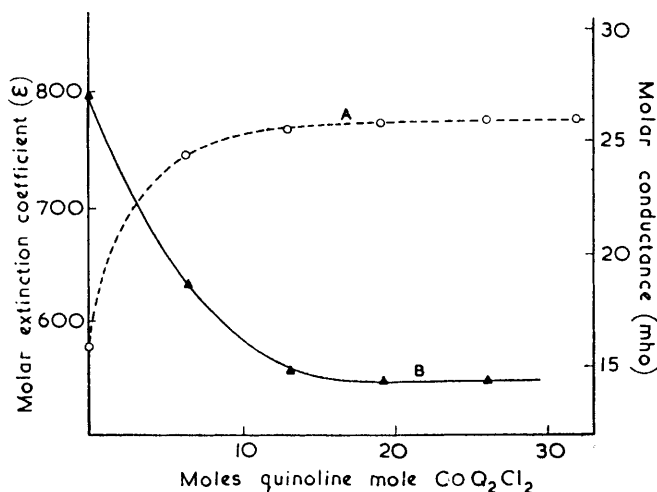
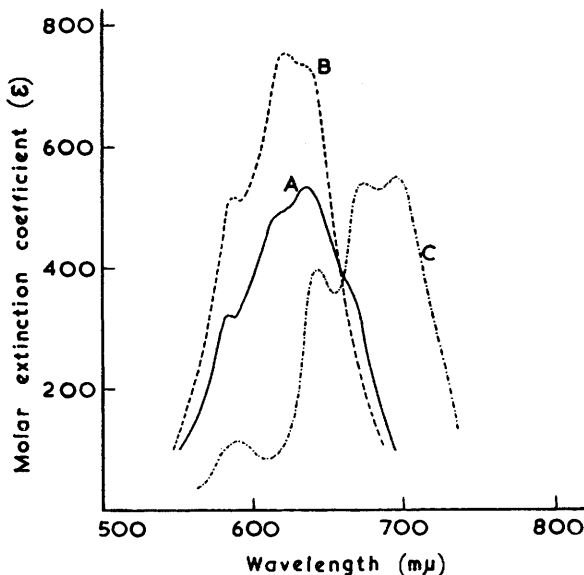


FIG. 2. Effect of added quinoline on apparent molar extinction coefficient (curve A) and electrical conductance (curve B) of 10^{-3}M - CoQ_2Cl_2 in nitromethane.

no appreciable change in apparent molar absorbance of any of the quinoline complexes in either nitromethane or chloroform was observed. This shows that there is little or no tendency for the octahedral tetrakisquinoline complex CoQ_4X_2 to be formed in solution. Similar effects were observed for CoQ_2I_2 , and to a less extent $\text{Co}(\text{IQ})_2\text{I}_2$, in nitromethane, though not in chloroform. For example, the 737 $\text{m}\mu$ band in the spectrum of CoQ_2I_2 in nitromethane which is suppressed on addition of quinoline, is the main feature of the spectrum of CoI_4^{2-} in the same solvent.¹ Although the tetrahedral absorption band was enhanced on addition of free amine for the other quinoline complexes, as well as the

chloride and iodide, no marked spectral profile changes were apparent, even for solutions of $\text{CoQ}_2(\text{NCS})_2$ and $\text{CoQ}_2(\text{NCSe})_2$ for which Beer's law deviations were particularly serious. This is not surprising since the spectra of $\text{CoQ}_2(\text{NCS})_2$ and $\text{Co}(\text{NCS})_4^{2-}$ are very similar, the absorption maxima of these two species occurring at 620—622 and 625—627 $\text{m}\mu$ ¹¹ respectively in nitromethane. As with the chloride the molar conductance at 20° of $10^{-3}\text{M-CoQ}_2(\text{NCS})_2$ in nitromethane fell from 40 mho to a fairly constant ~20 mho on addition of more than 25 moles of quinoline per mole of complex.

In contrast to the behaviour of the quinoline complexes the isoquinoline complexes, with the exception of $\text{Co}(\text{IQ})_2\text{I}_2$ in nitromethane, showed no sign of any substantial measure of decomposition in solution. Beer's law was obeyed closely in all cases. $10^{-3}\text{M-Co}(\text{IQ})_2\text{Cl}_2$ in nitromethane had a molar conductance of 6.3 mho, considerably less than for the corresponding quinoline complex, and on addition of isoquinoline the conductance did not decrease but slightly increased. Although a slight enhancement of the tetrahedral absorption on addition of small amounts of isoquinoline was usually observed in nitromethane, such effects were absent or very small in chloroform. In fact, with these solutions the effect of larger concentrations of added amine was to decrease the intensity of the tetrahedral band, and as the quantity of amine was progressively increased, to change the colour from blue (or green) to pale pink (or tan). Spectral examination of these solutions ($\epsilon = 5-10$) containing large excesses of amine (Table 2) indicated the presence of octahedrally co-ordinated cobalt species and from the close agreement of the positions of the spectral bands with those found for the solid $\text{Co}(\text{IQ})_4\text{X}_2$ complexes we conclude that the same molecules have been formed in solution. Thus it was evident that in solutions of isoquinoline complexes in chloroform containing free isoquinoline we were dealing with tetrahedral-octahedral equilibria of type (1). Equilibrium constants were determined

TABLE 3.

Thermodynamic data for the tetrahedral-octahedral equilibria in chloroform at 20°.

Complex	<i>K</i>	$-\Delta F$ (kcal. mole ⁻¹)	$-\Delta H$ (kcal. mole ⁻¹)	$-\Delta S$ (cal. deg. ⁻¹ mole ⁻¹)
$\text{Co}(\text{IQ})_2\text{Cl}_2$	9.78 (12.6)	1.32 ± 0.02 (1.48)	14.7 ± 0.3 (15.2)	45.7 ± 1.0 (46.8)
$\text{Co}(\text{IQ})_2\text{Br}_2$	7.27 (9.04)	1.16 ± 0.03 (1.28)	16.6 ± 0.3 (15.6)	52.7 ± 1.1 (48.8)
$\text{Co}(\text{IQ})_2\text{I}_2$	2.29 (2.32)	0.48 ± 0.03 (0.49)	17.4 ± 0.4 (16.6)	57.7 ± 1.5 (54.9)
$\text{Co}(\text{IQ})_2(\text{NCO})_2$	10.6 (23.3)	1.37 ± 0.03 (1.83)	— (13.7)	— (40.5)
$\text{Co}(\text{IQ})_2(\text{NCS})_2$	24,200 (83,000)	5.88 ± 0.04 (6.60)	— (16.6)	— (34.1)

spectrophotometrically at 20° as described in Part I. Heats of reaction were determined calorimetrically for the halide complexes at the same temperature and the corresponding entropy changes calculated (Table 3). Enthalpy changes are not available for the cyanato- or thiocyanato-complexes because the low solubility of the octahedral adducts in chloroform rendered accurate determination extremely difficult.

DISCUSSION

Solid octahedral complexes CoQ_4X_2 could not be prepared, nor was evidence found for their existence in solution, but for isoquinoline as ligand the co-ordination number of cobalt is not so limited. Since quinoline and isoquinoline have similar basicities ($\text{p}K_a = 4.85$ and 5.14 , respectively, at 20°)¹² the most obvious explanation is that substitution at the carbon atom alpha to the donor nitrogen atom introduces a steric barrier to the formation of an octahedral complex containing four quinolines. Exactly analogous behaviour was found previously for 2-methylpyridine complexes.¹ Steric effects in quinoline complexes requires further comment, however. Goodgame and Goodgame² reported their

¹² Brown, McDaniel, and Hatlinger, "Dissociation Constants," in Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, 1955.

failure to prepare $\text{NiQ}_4(\text{X})_2$ complexes ($\text{X} = \text{halide}$) but they considered that steric effects were unlikely to be important since Grossmann and Hunseler³ claimed to have prepared the corresponding thiocyanate, $\text{NiQ}_4(\text{NCS})_2$. The apparent stability and ease of formation of such a structure surprised us and we re-prepared Grossmann and Hunseler's compound as they described. A full description of the properties of this complex will be reported separately; however, preliminary analysis suggests that it is the dihydrate, $\text{NiQ}_4(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$.¹³ It is likely therefore that only two quinoline molecules are co-ordinated to the metal, the remaining two octahedral positions being occupied by the much smaller water molecules. All evidence, then, points to serious steric hindrance to the formation of tetrakisquinoline complexes. Indeed, the relative instability of the tetrahedral bisquinoline molecules in solution suggests that steric effects may be important here also.

Thermodynamic functions for the tetrahedral–octahedral equilibria of the isoquinoline complexes are in Table 3; the values in parentheses refer to the equilibria for the corresponding pyridine complexes.¹ For both series of complexes the dependence of the equilibrium constant on the anionic ligand X is the same, *i.e.*, K falls in the sequence $\text{NCS}^- \gg \text{NCO}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. In each case K is a little lower for the isoquinoline than for the pyridine complex. For the isoquinoline as for pyridine complexes both the heat of reaction ($-\Delta H$) and the entropy loss ($-\Delta S$) increase from chloride to bromide to iodide. In Part I it was suggested that these two effects have a common origin, an increase in the degree of d_π – p_π overlap in the metal–amine bond. Thus an increase in bond order, in the series $\text{Cl} < \text{Br} < \text{I}$, serves both to strengthen the bond and also to restrict free rotation about the bond, *i.e.*, to increase both $-\Delta H$ and $-\Delta S$. It seems that the extent of the π -orbital overlap depends on the polarisability of the halide ion; the more charge transferred from halide to metal the more easily does the metal release its non-bonding t_{2g} electrons for overlap with the antibonding π -orbitals of the heterocyclic aromatic amine. By analogy with the results obtained for the pyridine complexes the relatively high K observed for the isoquinoline–thiocyanate complex is probably due mainly to a more favourable entropy term which, in terms of this model, implies a smaller loss of free rotation about the metal–amine bond on formation of the octahedral complex, *i.e.*, less double-bonding. In Part I we suggested that this is because the NCS^- ion itself is a relatively good π -acceptor and, as a consequence, the non-bonding metal d orbitals are less available for overlap with heterocyclic amine π -orbitals.

Graddon and his co-workers¹⁴ question this interpretation¹ of the large difference in K and ΔS for the pyridine–halide and pyridine–thiocyanate complexes. They point out, correctly, that since the nitrogen atom (the co-ordinating atom of the NCS^- ion) is smaller than halide ions a smaller steric effect is to be expected in thiocyanato-complexes. However if only steric effects were important then K and ΔS for the cyanato- and thiocyanato-systems should be comparable, since nitrogen is the co-ordinating atom in each case. Further, $-\Delta H$ increases in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$, precisely as expected for an increasing π -contribution to the metal–amine bond but the opposite expected on purely steric grounds. We infer, therefore, that steric effects cannot be more than partly responsible for the observations.

TABLE 4.

X	$K_{\text{IQ}}/K_{\text{PY}}$	$-\Delta S_{\text{PY}}$ (cal. deg. ⁻¹ mole ⁻¹)	X	$K_{\text{IQ}}/K_{\text{PY}}$	$-\Delta S_{\text{PY}}$ (cal. deg. ⁻¹ mole ⁻¹)
NCS^-	0.29	34.1	Br^-	0.80	48.8
NCO^-	0.46	40.5	I^-	0.99	54.9
Cl^-	0.77	46.8			

Although K for reaction (1) is somewhat lower for $\text{L} = \text{isoquinoline}$ than for $\text{L} = \text{pyridine}$, we do not attach significance to the actual magnitude of the difference in K for any pair such as CoPy_2Cl_2 and $\text{Co}(\text{IQ}_2)\text{Cl}_2$. Such differences could arise from variations in

¹³ Nelson and Shepherd, unpublished work.

¹⁴ Graddon, Schulz, Watton, and Weedon, *Nature*, 1963, 198, 1299.

solvation effects due to change of amine. However, it probably is significant that the effect becomes noticeably smaller as we pass along the series of anionic ligands NCS^- , NCO^- , Cl^- , Br^- , I^- , because in comparing the relative magnitudes of the effect of replacing pyridine by isoquinoline in a series of complexes having different X ions we should be cancelling out whatever solvation effects a change in either X or amine gives rise to. In Table 4 we compare the ratio of the equilibrium constants for the two series of complexes, $K_{\text{IQ}}/K_{\text{PY}}$, with the entropy change for the reaction (pyridine series) for complexes with different ligands X. As the negative entropy change becomes larger so the ratio becomes larger. This correlation may be accounted for in terms of our model of a dependence of the degree of π -bonding in the metal-amine bond on the nature of the ligand partner X, as follows: isoquinoline is a weaker base (hydrogen-ion acceptor) than pyridine ($\text{p}K_{\text{a}} = 5.14$ and 5.23 , respectively¹²). Although we have no data for the enthalpy of protonation of isoquinoline in aqueous solution, information for pyridine and its alkyl derivatives suggests that $\text{p}K_{\text{a}}$ can be regarded as a measure of this function.¹⁵ If this is true for isoquinoline also then this amine must be considered a slightly weaker σ -donor than pyridine.* However, we would expect it to be better able to accept back-co-ordinated electrons on account of the more extensive delocalisation of its π -electrons. Therefore a metal-isoquinoline bond should be weaker than the corresponding metal-pyridine bond if it is predominantly σ in character, but this weakening of the bond should be at least partly offset if there is reason to expect a large π -component to the bond. If $K_{\text{IQ}}/K_{\text{PY}}$ is an indicator, this is essentially the situation we find for the complexes described here. Thus, in the thiocyanates, in which little π -overlap in the metal-amine bond is suggested, K falls from 83,000 to 24,200 on replacement of pyridine by isoquinoline. In the iodide complexes, however, in which we envisage a substantial measure of π -bonding, K remains virtually unchanged on amine replacement. It appears that as the π -component to the metal-amine bond is enhanced so also is the stability of the $\text{Co}(\text{IQ})_4\text{X}_2$ complex relative to CoPY_4X_2 . Further work on these effects is in progress.

Finally, whereas with the pyridine series there is a fairly good correlation between the configuration (tetrahedral or bridged-octahedral) of the solid complex and the equilibrium constant K of the tetrahedral-octahedral equilibrium in solution, with the isoquinoline complexes the solid state configuration is tetrahedral in all cases, even when K is large. The similarity of the thermodynamic functions for the solution equilibria for the two series indicates that the larger size of isoquinoline does not *substantially* alter the ease of formation of the mononuclear six-co-ordinate complex. This is evident also from molecular models. The failure of the metal in the bisoquinoline complexes (where K is large, e.g., $\text{X} = \text{NCS}^-$) to adopt a co-ordination number of six must then be due to greater difficulty in building a stable lattice for a bridged-octahedral structure. These results emphasise the need for caution in drawing conclusions about relative degrees of co-ordinative saturation of a metal ion from data on solid state stereochemistry alone.

EXPERIMENTAL

Preparation of Bisquinoline Complexes.— $\text{X} = \text{Cl}$ or Br . Hot ethanolic solutions of the hydrated dihalogenocobalt salt (1 mol.) and quinoline (~ 5 mol.) were mixed. On cooling the blue crystals separated. They were recrystallised from ethanol, washed with a little cold ethanol followed by carbon tetrachloride, and dried in air.

* *Note added in Proof.*—Recent work by Sacconi, Paoletti, and Ciampolini (*J. Amer. Chem. Soc.*, 1960, **82**, 3831) shows that the enthalpy of protonation of isoquinoline in aqueous solution is actually greater than that of pyridine, suggesting that isoquinoline and not pyridine may be the better σ -donor. Since hydration effects render the interpretation of the thermodynamic data for protonations in aqueous solution difficult it is probably better to consider the charge density on the nitrogen atom (Q_{N}) as a measure of σ -donor ability. For isoquinoline and pyridine Q_{N} is the same (Brown and Dewar, *J.*, 1953, 2406). In any case, whatever the relative σ -donor powers of isoquinoline and pyridine, our argument for a greater π -acceptor capacity for isoquinoline remains unaffected.

¹⁵ Dickens, D.Phil. Thesis, Oxford, 1954.

X = I, NCS, NCSe. Ethanolic solutions of hydrated cobalt nitrate (1 mol.) and KX (2 mol.) were mixed and the precipitated potassium nitrate filtered off. The solution was evaporated somewhat under an infrared lamp and filtered directly into an ethanolic solution of quinoline (~5 mol.). The product separated on standing and was recrystallised from ethanol.

X = NCO. Cold aqueous solutions of cobalt nitrate (1 mol.) and potassium cyanate (2 mol.) were mixed and aqueous ethanolic quinoline (~2.5 mol.) added. The mixture was well shaken and the deep blue crystalline complex which rapidly separated was washed well with water and ethanol and recrystallised from ethanol. Infrared analysis indicated the absence of carbonate.

Tetrakisquinoline Complexes. X = Cl, Br. Hot ethanolic solutions of the hydrated dihalogenocobalt salt (1 mol.) and isoquinoline (~5 mol.) were mixed. Pink crystals of $\text{Co}(\text{IQ})_4\text{X}_2$ quickly separated. The product was washed with a little cold ethanol and recrystallised from ethanol containing isoquinoline.

X = I, NCS, NCSe. The procedure was analogous to that for CoQ_2I_2 etc. The products were pink, or tan, crystals.

X = NCO. This pink complex was prepared as described for $\text{CoQ}_2(\text{NCO})_2$ except that 5 mol. proportions of isoquinoline were used.

Bisisoquinoline Complexes.—X = Cl, Br, I, NCO. The appropriate tetrakisquinoline complex was refluxed for about 1 hr. with carbon tetrachloride and the hot suspension filtered. The process was repeated several times. The blue or green (X = I) product was recrystallised from ethanol.

X = NCS. $\text{Co}(\text{IQ})_4(\text{NCS})_2$ was repeatedly refluxed with ethanol, and the blue product which still contained a little $\text{Co}(\text{IQ})_4(\text{NCS})_2$ carefully heated at 50–60° for 2 hr.

X = NCSe. Attempts to obtain this complex from $\text{Co}(\text{IQ})_4(\text{NCSe})_2$ by either of the above methods were unsuccessful. The isoquinoline seems to be strongly bound and cannot be removed at a temperature below the decomposition point of the selenocyanate group.

Each of the complexes was analysed for cobalt by EDTA titration in hexamine-buffered solution with methyl thymol blue metal indicator at 40°. In every case observed analyses agreed with the calculated values to better than $\pm 0.05\%$.

Measurement of Equilibrium Constants.—These were done spectrophotometrically by a method similar to that described previously.¹ AnalaR chloroform used as solvent was dried (molecular sieve) and distilled. Quinoline and isoquinoline were fractionally distilled under reduced pressure. For halide and cyanate complexes, where K is small, an improved method of calculation was used which does not necessitate a precise knowledge of the concentration of the complex in solution. The optical densities (D^1) at the wavelength of maximum absorption of a series of solutions of different concentrations of the bisoquinoline complex, each containing the same accurately known excess of isoquinoline, were measured at 20°. The optical densities (D^0) of the same series of solutions but without added isoquinoline were also measured. When the quantity of isoquinoline consumed in forming the octahedral adduct is small compared with the total quantity present, *i.e.*, when K is small, then the plot of D^1 against D^0 is linear, of slope $(KB^2 + 1)$ where B is the concentration of the added isoquinoline. In practice a small amount of isoquinoline was added to the chloroform used for the D^0 determinations to suppress any slight disproportionation that might have occurred in dilute solution. Control experiments showed that where K is small the quantity added (~10⁻³ mole per litre) is much less than that required to cause any significant conversion of the tetrahedral complex into the octahedral adduct; no measurable error in the determination of K was therefore introduced. For the thiocyanato-complex for which K is large, the appropriate correction was applied. The values of K in Table 3 are the averages of several independent determinations.

The calorimetric, magnetic, and electrical conductance measurements were as described previously.

One of us (E. K.) acknowledges study leave from the L. Eötvös University of Budapest, and a Research Fellowship from the Queen's University of Belfast.

DEPARTMENT OF CHEMISTRY,
THE QUEEN'S UNIVERSITY OF BELFAST.

[Received, February 3rd, 1964.]