596. *The Co-ordination Number of Transition-metal Ions. Part III.*[1] *Complexes of Nickel*(II) *Halides with Heterocyclic Aromatic Amines*

By S. M. NELSON and T. M. SHEPHERD

The magnetic and electronic spectral properties of a series of (in many cases) new complexes of the general type NiL_nX_2 are reported (L = pyridine, β-picoline, γ-picoline, or isoquinoline; X = Cl, Br, I, or NCS; n = 1, 2, or 4). An assignment of the spectra of the tetrakisamine complexes, NiL_4X_2 (X = halide), in terms of D_{4h} symmetry is suggested. Of the bisamine complexes, NiL_2X_2, all except the iodides (which are pseudo-tetrahedral) have 6-co-ordinate structures comprising bridging X groups. The spectra suggest that in these the ligand field is less asymmetric than in the NiL_4X_2 series. Comparisons are also made with complexes containing ammonia as ligand. The results are discussed in terms of varying degree of metal-ligand π-bonding.

A polymeric structure is suggested for the $NiLX_2$ series of complexes in which the ligand field around the metal atom arises from five X ions and one nitrogen atom.

IN Parts I[2] and II[1] of this Series we reported the results of a thermodynamic investigation of a configurational equilibrium between tetrahedral cobalt(II) complexes of the type CoL_2X_2, and the corresponding octahedral adducts, CoL_4X_2, in chloroform solution containing excess of L (L = heterocyclic aromatic amine and X = halide or pseudo-halide ion). It was shown that the nature of both L and X has a striking effect on the relative stabilities of the tetrahedral and octahedral states, and from an analysis of the thermodynamic data it was suggested that the nature of X can strongly influence the extent of dative d_π–p_π bonding in the cobalt–amine bond. It was of interest to extend the studies to analogous complexes of nickel(II). A considerable number of complexes of nickel(II) salts with heterocyclic aromatic amines have been investigated previously. Those with pyridine,[2-4] sterically hindered pyridines (α-picoline,[4] quinoline,[5] α-lutidines[6]) and pyrazines[7] having received particular attention. A variety of solid-state structures (octahedral, tetrahedral, planar) have been found and in some cases structural isomers identified. As with cobalt(II) complexes it seems that the energy separation of different structural forms is often quite small and that stereochemical changes can be brought about by minor changes in the nature of the co-ordinating atoms or groups. The importance of steric effects in limiting co-ordination number has been emphasised. However, little attempt has yet been made to account for the dependence of stereochemistry on other ligand properties in this class of nickel(II) complex. It was the purpose of the work to be described here to examine how far the conclusions of Parts I and II might be useful in this respect. It was also of interest to examine the electronic effect of the nature and position of the substituent in complexes with non-sterically hindered pyridine derivatives. Recent work in these laboratories on cobalt(II) complexes of this type has suggested that not only the basic strength of the amine but also the π-acceptor properties may be significantly altered by substitution.[8] The recent results of Quagliano and his co-workers[6] on nickel(II)–lutidine complexes underline also the importance of electronic factors. The complexes studied here are of the general type NiL_nX_2 where L = pyridine, β-picoline, γ-picoline, or isoquinoline; X = Cl, Br, or I, and in some cases, NCS; n = 4, 2, or 1.

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[1] Part II, H. C. A. King, E. Körös, and S. M. Nelson, *J.*, 1964, 4832.

[2] H. C. A. King, E. Körös, and S. M. Nelson, *J.*, 1963, 5449.

[3] N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88.

[4] M. D. Glonek, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.

[5] D. M. L. Goodgame and M. Goodgame, *J.*, 1963, 207.

[6] S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, 1964, **3**, 480, 671.

[7] A. P. B. Lever, J. Lewis, and R. S. Nyholm, *J.*, 1963, 5042.

[8] H. C. A. King, S. M. Nelson, and T. M. Shepherd, unpublished work.

Structural analysis is based mainly on spectral and magnetic properties. No attempt was made to prepare all the complexes theoretically obtainable from these combinations of ligands.

RESULTS

NiL_4X_2 *Complexes.*—Three of these, Nipy$_4$Cl$_2$, Nipy$_4$Br$_2$, and Nipy$_4$(NCS)$_2$ (py = pyridine) are known from *X*-ray analysis to have six-co-ordinate structures in which the anionic ligands are in *trans*-positions.[9] There seems little reason to doubt that all the complexes of this stoicheiometry examined here have mononuclear six-co-ordinate structures. This expectation is confirmed by a study of their magnetic and electronic spectral properties. In all cases the room temperature magnetic moments (Table 1) fall within the range, 2·83—3·4 B.M., expected for six-co-ordinate spin-free nickel(II).[10] Table 2 gives the electronic spectra both of the solid and of solutions. The spectra of solutions were measured in chloroform containing ~5% excess of the appropriate amine. The addition of free amine was necessary in all cases in order to suppress dissociation of the complex to NiL_2X_2 (and probably related ionic species also) and free amine. Similar effects have been observed by Quagliano and his co-workers in dichloromethane solutions of tetralutidinenickel(II) complexes.[6] Reflectance specta are in the range 10,000—28,000 cm.$^{-1}$; for the solution measurements the range could be extended to 5000 cm.$^{-1}$ on the low frequency side. The spectra of the solid and solution are closely similar in the 10,000—28,000 cm.$^{-1}$ range, indicating that under the conditions employed no observable decomposition occurs on dissolution. With the exception of the thiocyanato-complexes the spectra all have three features in common (see Figure 1). These are a sharp band (masked in the case of the iodo-complexes by a strong charge transfer absorption) of maximum extinction, ε = 15—20, at about 25,000 cm.$^{-1}$, a second broader, usually unsymmetrical band (ε = 6—12) at 15,000—16,000 cm.$^{-1}$, and a third weak absorption at ~11,000 cm.$^{-1}$). In each case there is also a broad band at lower energies which is dependent on the nature of the halide. Bostrup and Jørgensen[11] have previously assigned the 10,900 and 8500 cm.$^{-1}$ bands in Nipy$_4$Cl$_2$ as the components of

TABLE 1

Magnetic data for NiL_nX_2 complexes

Complex	Colour	Magnetic moment (B.M.)	Temp.	Complex	Colour	Magnetic moment (B.M.)	Temp.
	(*a*) NiL_4X_2				(*b*) NiL_2X_2		
Nipy$_4$Cl$_2$	Pale blue	3·11	15·8	Nipy$_2$Cl$_2$	Pale green	3·39	20·0
Ni(β-pic)$_4$Cl$_2$	,,	3·19	18·0	Ni(β-pic)$_2$Cl$_2$	,,	3·45	17·9
Ni(γ-pic)$_4$Cl$_2$	,,	3·16	17·8	Ni(γ-pic)$_2$Cl$_2$	,,	3·35	15·2
Ni(I–Q)$_4$Cl$_2$	,,	3·20	18·1	Ni(I–Q)$_2$Cl$_2$	,,	3·40	17·2
Nipy$_4$Br$_2$	Blue-green	3·22	17·2	Nipy$_2$Br$_2$	Yellow-green	3·35	18·1
Ni(β-pic)$_4$Br$_2$	,,	3·14	18·0	Ni(β-pic)$_2$Br$_2$	,,	3·25	17·5
Ni(γ-pic)$_4$Br$_2$	,,	3·11	17·5	Ni(γ-pic)$_2$Br$_2$	,,	3·34	14·4
Ni(I–Q)$_4$Br$_2$	,,	3·13	16·0	Nipy$_2$I$_2$	Dark green	3·44[4]	~20·0
NipyI$_2$	Yellow-green	3·21	17·0	Ni(β-pic)$_2$I$_2$	,,	3·21	~20·0
Ni(β-pic)$_4$I$_2$	,,	3·12	21·0	Ni(γ-pic)$_2$)$_2$	,,	3·35	15·9
Ni(γ-pic)$_4$I$_2$	,,	3·18	14·9	Ni(NH$_3$)$_2$Cl$_2$	Pale green	3·35[14]	20·0
Ni(I–Q)$_4$I$_2$	,,	3·07	15·4	Ni(NH$_3$)$_2$Br$_2$	Yellow-green	3·29[14]	20·0
	(*c*) $NiLX_2$						
NipyCl$_2$	Pale yellow	3·47	18·0				
Ni(β-pic)Cl$_2$	,,	3·30	15·4				
Ni(γ-pic)Cl$_2$	,,	3·47	14·4				
NipyBr$_2$	Yellow-orange	3·41	18·0				
Ni(β-pic)Br$_2$	Red	3·25	17·5				
Ni(γ-pic)Br$_2$	Yellow-orange	3·38	14·6				

py = Pyridine; β-pic = β-picoline; γ-pic = γ-picoline; I–Q = *iso*quinoline

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[9] M. A. Porai-Kojie, A. S. Antzishkina, L. M. Dickareva, and E. K. Jukhov, *Acta Cryst.*, 1957, **10**, 784.

[10] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publ., Inc., New York, 1962, p. 738.

[11] O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

TABLE 2

Electronic absorption spectra of NiL_4X_2 complexes

Complex	State	$\lambda_{max.}$ (cm.$^{-1}$) (ε_{molar} for solutions)
$Nipy_4Cl_2$	Solid	25,640, 15,800, ~10,800
	Soln.*	25,500(12·5), 15,820(5·5), ~14,000sh, 12,600w, 10,900, 8500(5·0)
$Ni(\beta\text{-pic})_4Cl_2$	Solid	25,300, 15,750, ~14,300sh
	Soln.*	25,800(12·5), 15,700(5·3), 14,000sh, 12,600w, 11,600—10,500, 8400(5·0)
$Ni(\gamma\text{-pic})_4Cl_2$	Solid	25,640, 15,900, ~14,300sh
	Soln.*	25,700(15·0), 15,820(8·0), 14,000sh, 12,600, 10,900, 8350(4·0)
$Nipy_4Br_2$	Solid	25,300, 20,700w, 15,620, ~12,300, 11,200, 10,600—10,200
	Soln.*	25,150(16·2), 20,200vw, 15,700(6·0), ~12,400sh, 11,200, 7800(5·0)
$Ni(\beta\text{-pic})_4Br_2$	Solid	25,300, 20,400w, 15,800, ~11,500w
	Soln.*	25,400(17·0), ~20,500w, 15,770(5·8), 12,400sh, 11,100w, 7800(5·5)
$Ni(\gamma\text{-pic})_4Br_2$	Solid	25,300, 15,800, ~12,300 sh
	Soln.*	25,250(17·0), ~20,400 sh, 15,770(6·5), 12,400sh, ~11,100w, 7720
$Nipy_4I_2$	Solid	26,000, ~23,300sh, ~19,200sh, 15,870, 13,200—12,500w, ~11,100
	Soln.*	25,640, 15,700(9·4), ~11,100w, 7350(9·0)
$Ni(\beta\text{-pic})_4I_2$	Solid	25,600, ~23,300sh, 16,050, 13,000—10,000 not resolved
	Soln.*	25,800, 15,970(8·3), 11,500—10,700w, 7340(8·0)
$Ni(\gamma\text{-pic})_4I_2$	Solid	26,300, ~23,300sh, ~19,000sh, 15,900, ~14,700sh
	Soln.*	18,870sh, 16,030(9·5), 13,200—11,600, 11,050sh, 7350(8·5)
$Nipy_4(NCS)_2$	Solid	27,200, ~22,200sh, 16,900, 12,800sh, 10,450
	Soln.*	27,400, 22,200sh, 16,900, ~12,800sh, 10,480
$Ni(\beta\text{-pic})_4(NCS)_2$	Solid	27,000sh, ~22,500w, 16,900, ~12,700sh, 10,400
	Soln.*	27,200sh, 22,500w, 16,900, ~12,800sh, 10,400
$Ni(\gamma\text{-pic})_4(NCS)_2$	Solid	27,000sh, 22,500w, 17,100, 12,700sh, 10,500
	Soln.*	27,200, 22,500, 17,060, ~12,900sh, 10,450

* $2·5 \times 10^{-2}$M in dried, redistilled AnalaR grade $CHCl_3$ containing 5% added amine at 20°.

the ν_1 transition [$^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ in O_h symmetry] which is split due to tetragonal distortion. A similar assignment may be made for the bromo- and iodo-complexes where in each case the 11,000 cm.$^{-1}$ band is the higher energy component, and the lower energy component is at 7800 cm.$^{-1}$ in the bromides, and at 7200 cm.$^{-1}$ in the iodides. Accepting this assignment the separation of the two split components of ν_1 can be seen to vary with the co-ordinated halide, increasing from ~2500 cm.$^{-1}$ for the chlorides to ~3300 cm.$^{-1}$ for the bromides and ~3800 cm.$^{-1}$ for the iodides. The energy separation may be taken as a measure of the degree of tetragonal distortion which as one would expect increases as the ligand field strength of the halide ion departs more from that of the aromatic amine. In D_{4h} symmetry the split components of the $^3T_{2g}$ level thus become ^3E_g and $^3B_{2g}$ with a separation equal to $(35/4)Dt$.[12] However ν_2 and ν_3 would also be expected to show splittings equal to 6 $Ds(5/4)Dt$ and $5Dt - 3Ds$, respectively.[12] Any splitting there may be in these bands is not resolved. However, the 15,000—16,000 cm.$^{-1}$ band is somewhat unsymmetrical on the low-frequency side. For example in $Nipy_4Cl_2$ there is a shoulder at ~14,300 cm.$^{-1}$. If this band is taken as the low frequency component of a split ν_2 then the splitting is equal to ~1500 cm.$^{-1}$.

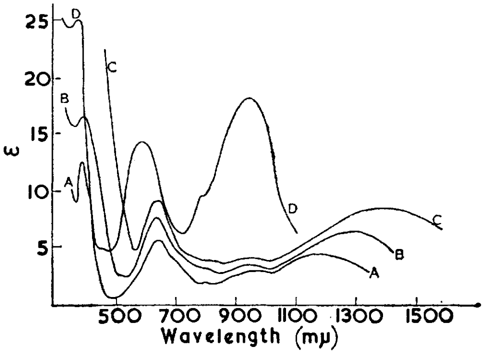

FIGURE 1. Spectra of $Nipy_4X_2$ complexes in chloroform containing 5% added pyridine

(A) X = Cl
(B) X = Br
(C) X = I
(D) X = NCS

While the spectra of the halide complexes are best interpreted in terms of D_{4h} symmetry the extent of tetragonal distortion in the thiocyanato-complexes is much less. Here, as was previously found for one of them, $Nipy_4(NCS)_2$,[11] no splitting of the lowest energy triplet

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[12] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, 1964, **40**, 788.

transition ν_1 is observed, and there is good agreement between the observed and calculated band positions for $10Dq$ ($= \nu_1$) = 10,400—10,500 cm.$^{-1}$.* The absence of any severe tetragonal distortion may be attributed to the more nearly symmetrical ligand field since nitrogen co-ordinated NCS and pyridine (or its derivatives) occupy positions fairly close to each other in the spectrochemical series.[11] It is interesting that β-picoline appears to exert a slightly weaker ligand field than the other amines studied here.

NiL_2X_2 *Complexes.*—The configurations of four solid complexes of this stoicheiometry have been determined previously. $Nipy_2Cl_2$ and $Nipy_2Br_2$ have polymeric structures containing six-co-ordinate nickel atoms and bridging halide atoms.[2,3] Tetrahedral structures have recently been suggested for $Nipy_2I_2$ and Ni(β-pic)$_2$I$_2$.[4] The remainder have not been examined previously. The temperature magnetic moments (Table 1) at room temperature all fall within the range 3·27—3·45 B.M., and thus have little diagnostic value in distinguishing between spin-free six-co-ordinate nickel(II) and tetrahedral nickel(II) complexes in which there are low-symmetry components to the ligand field. However, structural assignments may be made on the basis of the positions and intensities of the electronic spectral bands (see Tables 3 and 4). Only one of the previously unexamined complexes, Ni(γ-pic)$_2$I$_2$, appears to have a non-centrosymmetric structure. The electronic spectrum of this compound is practically identical to its

TABLE 3

Diffuse reflectance spectra for polymeric NiL_2X_2 and $NiLX_2$ complexes

Complex	Assignment ${}^3A_{2g}$)			
	${}^3T_{1g}(P)$	${}^1T_{2g}(D)$	${}^3T_{1g}(F)$	${}^1E_g(D)$
(*a*) NiL_2X_2.	Absorption max. (cm.$^{-1}$)			
$Nipy_2Cl_2$	24,100	$\sim$22,000sh	13,990	$\sim$12,500sh
Ni(β-pic)$_2$Cl$_2$	24,270	$\sim$22,000sh	14,180	$\sim$12,300sh
Ni(γ-pic)$_2$Cl$_2$	23,980	$\sim$21,800sh	13,950	$\sim$12,400sh
Estimated for Dq = 850 cm.$^{-1}$...	24,000	21,000	13,500—14,500	12,400
$Nipy_2Br_2$	23,530	$\sim$20,000sh	13,850	$\sim$11,900sh
Ni(β-pic)$_2$Br$_2$	23,420	$\sim$20,000sh	13,330	$\sim$11,900sh
Ni(γ-pic)$_2$Br$_2$	23,420	$\sim$19,600sh	13,760	$\sim$12,100sh
Estimated for Dq = 820 cm.$^{-1}$...	23,500	20,000	13,000—14,000	12,200
$Ni(NH_3)_2Cl_2$	24,800	$\sim$22,900sh	13,600	$\sim$12,000sh
$Ni(NH_3)_2Br_2$	23,800		13,120	$\sim$11,600sh
(*b*) $NiLX_2$				
$NipyCl_2$	22,520		12,990, 12,240	$\sim$11,800sh
Ni(β-pic)Cl$_2$............	22,420	$\sim$19,000sh	13,050, 12,240	$\sim$11,900sh
Ni(γ-pic)Cl$_2$............	22,470	$\sim$19,000sh	12,990, 12,400	$\sim$11,900sh
$NipyBr_2$	21,370	$\sim$18,200sh	12,380, 11,800	$\sim$10,800sh
Ni(β-pic)Br$_2$	20,530	$\sim$18,000sh	11,630	$\sim$10,400sh
Ni(γ-pic)Br$_2$	21,370	$\sim$18,200sh	12,440, 11,700	$\sim$10,900sh
(*c*) NIX_2				
$NiCl_2$	22,100	$\sim$19,400	12,900	$\sim$11,600
$NiBr_2$	20,700	$\sim$17,500	12,100	$\sim$10,300

TABLE 4

Electronic absorption spectra for tetrahedral NiL_2X_2 complexes

Complex	State	Absorption max. (cm.$^{-1}$) (ε molar for solutions)
Ni(β-pic)Br$_2$	Solid	See Table 3
	$CHCl_3$ soln.*	23,040, 18,350(90), 17,200sh, $\sim$11,760sh, 10,390(50)
	CH_3NO_2 soln.*	26,320, $\sim$18,350sh, 17,060(150), $\sim$11,760sh, 10,310(60)
$Nipy_2I_2$	Solid	25,640, 22,200, 16,670, 10,870, 10,200
	$CHCl_3$ soln.*	16,950(300), 10,870, 10,200
	CH_3NO_2 soln.*	25,910, $\sim$17,860sh, 17,060(118), $\sim$10,600sh, 10,000
Ni(β-pic)$_2$I$_2$	Solid	22,200, 16,670, $\sim$15,870sh, 10,810, 10,100
	$CHCl_3$ soln.*	16,890(330), 10,780, 10,000
	CH_3NO_2 soln.*	25,580, 16,950(161), 10,750, 10,000
Ni(γ-pic)$_2$I$_2$	Solid	25,640, 22,200, 16,390, 10,810, 10,050
	$CHCl_3$ soln.*	24,810, 21,930, 16,890(330), 10,810, 9950
	CH_3NO_2 soln.*	25,640, $\sim$22,730sh, 19,600, 16,920(210), 10,810, 9950

* 2·5 × 10^{-3}M in dried redistilled AnalaR grade solvent at 20°.

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* Bostrup and Jørgensen [11] report $10Dq$ = 10,200 cm.$^{-1}$ for $Nipy_4(NCS)_2$.

pyridine and β-picoline analogues, not only with respect to band position but also band intensity, which is relatively high in all cases. The low moments of all three-iodo-complexes suggest deviation from regular T_d symmetry, a view which is supported by the observed splitting of the band at ~17,000 cm.$^{-1}$ which in T_d symmetry would arise from the transition $^3T_1(F) \longrightarrow {}^3T_1(P)$.

Spectra of the three pseudo-tetrahedral iodo-complexes taken in chloroform or benzene solution are almost identical with those of the solid. Extinction coefficients of the ~17,000 cm.$^{-1}$ band are about 300—330. It would seem that little or no decomposition occurs on dissolution in these solvents. Extinction coefficients for solutions in nitromethane are much lower, however, and on adding iodide ion (as LiI) it was found that a marked rise in ε occurred, *e.g.*, in the case of a $2{\cdot}5 \times 10^{-3}$M solution of $Nipy_2I_2$, ε for the 17,060 cm.$^{-1}$ band increased from 120 to 230 on addition of excess of lithium iodide. Partial decomposition into free iodide ions and other ionic species in nitromethane solution was shown also by the high electrical molar conductance of solutions of these complexes which were of the order of 40—50 mho. Also supporting this view is the observation that Beer's law is not obeyed for nitromethane solutions. In contrast, Beer's law is obeyed for chloroform solutions, and spectrophotometric experiments indicated the establishment of a tetrahedral–octahedral equilibrium in such solutions containing an excess of the appropriate amine.

The remaining NiL_2X_2 complexes, where X = Cl or Br, are assigned a polymeric structure comprising bridging halide ions. The assignment follows from a consideration of the stoicheiometry, the magnetic moments, and spectra of solids, as well as by analogy with $Nipy_2Cl_2$. The moments fall in the range expected for octahedral co-ordination though there is a significant increase of 0·1—0·3 B.M. as compared with the corresponding mononuclear octahedral complexes, NiL_4X_2. However, the evidence for a centrosymmetric structure rests mainly on the low absorption intensities of the electronic spectral bands. The spectra are all of the same type. In each case (see Table 3) there is a band maximum at ~24,000 cm.$^{-1}$ (chlorides) or ~23,500 cm.$^{-1}$ (bromides) with a shoulder on the low-frequency side, and another band maximum at ~14,000 cm.$^{-1}$ (chlorides) or 13,300—13,700 cm.$^{-1}$ (bromides), again with a shoulder on the low frequency side. The spectra are very similar in form to those of anhydrous $NiCl_2$ and $NiBr_2$ (see Tables 3 and Figure 2), which are known to have regular octahedral structures.[11] It was of interest, therefore, to compare the band positions with those expected for transitions between electronic states with O_h symmetry using the energy level diagram of Liehr and Ballhausen.[13] Table 3 shows reasonably good agreement in most cases for $Dq \approx 850$ cm.$^{-1}$ (chlorides) and $Dq \approx 820$ cm.$^{-1}$ (bromides). This suggests that although the complexes belong to the molecular point group D_{4h} the electronic asymmetry of the ligand field

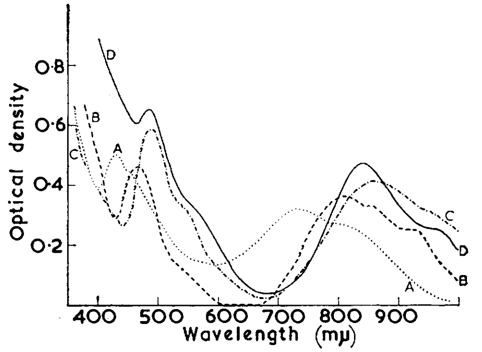

FIGURE 2. Reflectance spectra of NiL_2X_2, $NiLX_2$, and NiX_2
(A) $Nipy_2Br_2$
(B) $NipyBr_2$
(C) $Ni(\beta\text{-pic})Br_2$
(D) $NiBr_2$

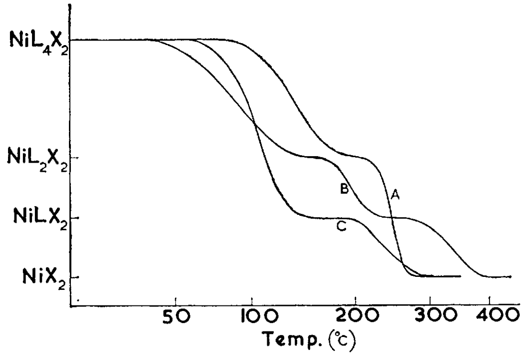

FIGURE 3. Thermograms of NiL_4X_2 complexes
(A) $Nipy_4(NCS)_2$
(B) $Nipy_4Br_2$
(C) $Ni(\gamma\text{-pic})_4Cl_2$

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[13] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (*N.Y.*), 1959, **6**, 134.

is not too serious.* Table 3 includes also corresponding data for the complexes $Ni(NH_3)_2Cl_2$ and $Ni(NH_3)_2Br_2$ prepared by Klemm and Schuth[14] for which no spectra have previously been reported. The moments (3·35 and 3·29 B.M. at 20°, respectively[14]) and the close similarity of the spectra with those of the bispyridine complexes indicate similar polymeric octahedral structures.

Further support for a structure comprising chains of bridged octahedra is provided by the observation that this group of complexes is generally poorly soluble in solvents of low polarity, in contrast to the ready solubility of the tetrahedral iodides. The β-picoline and γ-picoline complexes are more soluble than the corresponding pyridine complexes and the bromides more soluble than the chlorides. Most dissolve in nitromethane, acetone, and in chloroform to some extent, to give violet (chlorides) or blue-violet (bromides) solutions. The high absorption intensities of these solutions suggested the presence of tetrahedral or pseudotetrahedral species. The spectral bands of $Ni(\beta\text{-pic})_2Br_2$ (the most soluble of the polymers) in chloroform and nitromethane solution are listed in Table 4. The positions of the two principal bands at 17,060 and 10,300 cm.$^{-1}$ are consistent with electronic transition between the states $^3T_1(F) \longrightarrow {}^3T_1(P)$ and $^3T_1(F) \longrightarrow {}^3A_2$, respectively, though the broadness of the high frequency absorption suggests some crystal field splitting as a result of the asymmetry of the field. The weak absorption at ~11,800 cm.$^{-1}$ is probably due to the spin-forbidden transition to the singlet state $^1T_2(D)$. The relatively low electrical conductance ($\Lambda_M = 11{\cdot}5$ mho in $2{\cdot}5 \times 10^{-3}$M-nitromethane solution) indicates that the principal absorbing species is probably $Ni(\beta\text{-pic})_2Br_2$. However, there are significant differences in the spectra of $Ni(\beta\text{-pic})_2Br_2$ in nitromethane and chloroform solution. In addition to the slight profile changes in the 17,000—18,500 cm.$^{-1}$ absorption, there is a well-defined band at 23,040 cm.$^{-1}$ in chloroform solution which is absent in nitromethane solution. The intensity of this band was found to fall with rise in temperature whereas that of the maximum at 18,350 cm.$^{-1}$ increases. It seems there are species other than tetrahedral $Ni(\beta\text{-pic})_2Br_2$ present in chloroform solution, their concentration decreasing with rise in temperature.

$NiLX_2$ *Complexes*.—Six compounds of this type (where X = Cl or Br) have been prepared. Their existence was first indicated by thermogravimetric analysis of the corresponding NiL_4X_2 species which in every case examined showed a distinct break at this stoicheiometry; $Nipy_4(NCS)_2$, on the other hand, did not (see Figure 3). One of these compounds, $NipyCl_2$, has been prepared recently by Sharp and his co-workers[15] who state that thermal decomposition of other pyridinenickel halides does not proceed by way of the monopyridine complexes. In disagreement with this, our results show that $NipyBr_2$ can also be readily prepared in this way. Analogous complexes containing ammonia have been reported by Klemm and Schuth.[14]

While the thermograms of all the chlorides and bromides examined showed definite breaks at the $NiLX_2$ stoicheiometry, the γ-picoline complexes showed no discontinuity at NiL_2X_2. However, this cannot be taken as evidence for the non-existence of the compound at lower temperatures since we were able to prepare stable $Ni(\gamma\text{-pic})_2(Hal)_2$ complexes by other methods (see Experimental section).

The diffuse reflectance spectra (25,000—10,000 cm.$^{-1}$) are similar both to those of the bisamine chlorides and bromides and also to those of the anhydrous nickel salts (see Table 3 and Figure 2), the bands falling at intermediate wavelengths in most cases and by analogy with these we have, to a first approximation, assigned the bands as shown in Table 3. These are the same assignments proposed by Sharp and co-workers[15] for $NipyCl_2$. In our case, however, we find that the bands fall at slightly longer wavelengths. In contrast to the bisamine complexes, however, the ν_2 band in the $NiLX_2$ series shows a shoulder at energies ~600 cm.$^{-1}$ lower than the maximum. Possibly there is some splitting of ν_2 due to distortion. Unfortunately we were unable to obtain solid state spectra at frequencies lower than 10,000 cm.$^{-1}$

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* [*Note Added in Proof.*—In a very recent publication (*J.*, 1964, 5194) Goodgame, Goodgame, and Weeks reported the electronic spectra of a few of these complexes. They assign the shoulders on the ν_2 and ν_3 bands as spin allowed transitions to components of the $^3T_{1g}(F)$ and $^3T_{1g}(P)$ levels in D_{4h} symmetry. Thus, splittings of up to 2000 cm.$^{-1}$ were assumed. Such large splittings in these levels seem unlikely; they are not shown by the NiL_4X_2 complexes which, as judged by the splitting in ν_1, are even more tetragonally distorted. Moreover, since the spectra of anhydrous $NiCl_2$ and $NiBr_2$, which have regular octahedral structures, also show shoulders at corresponding positions we prefer to assign these absorptions in all cases to spin forbidden transitions.]

[14] W. Klemm and W. Schuth, *Z. anorg. Chem.*, 1933, **210**, 33.

[15] D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1067.

so it was not possible to estimate the splitting, if any, of ν_1. The magnetic moments (Table 1) are in all cases consistent with centrosymmetric six-co-ordination of the metal atom. As with the bisamine chlorides and bromides the orbital contributions are again unusually high.

DISCUSSION

The data demonstrate the result, now well established, that nickel(II) shows a marked preference for an octahedral, as compared with a tetrahedral, environment.* This is in contrast to cobalt(II) for which tetrahedral complexes containing heterocyclic aromatic amines are very common. Of all the known tetrahedral NiL_2X_2 complexes, where L = pyridine or substituted pyridine, all but a few contain a sterically hindered pyridine (α-picoline,[4] α-lutidine,[6] quinoline [5]). Moreover, there are few cases of six-co-ordinate nickel(II) complexes containing a sterically hindered pyridine. An example is the yellow form of $Ni(quinoline)_2Cl_2$ described by Goodgame and Goodgame.[5] However, comparison of the diffuse reflectance spectrum of this complex with those of analogous NiL_2Cl_2 compounds in which L is not sterically hindered (Table 3) shows that in the former compound the spectral bands lie at slightly longer wavelengths suggesting a weaker average ligand field. This could arise from a lengthening of the metal-ligand bonds as a consequence of inter-ligand repulsions. A similar explanation has been suggested recently to account for the spectra of some nickel(II) complexes containing sterically hindered pyrazines.[7] Support for the view that ortho substitution in the pyridine ring introduces a steric barrier to the attainment of six co-ordination by the metal is provided by the observation that in no case was it possible to prepare the corresponding mononuclear NiL_4X_2 complexes with L = α-picoline,[4] quinoline,[5] or α-lutidine.[6]

In the remaining tetrahedral NiL_2X_2 complexes (L = py, β-pic, γ-pic, X = I) there can be no steric hindrance to six co-ordination since (i) the corresponding NiL_4X_2 species are easily formed and stable, and (ii) stable bridged octahedral nickel(II) iodide complexes are known, *e.g.*, $Ni(pyrazine)_2I_2$,[7] containing neutral ligands of closely similar size and shape to pyridine. It follows that the iodo-complexes are tetrahedral for electronic reasons, probably being the high polarisability of the iodide ion coupled with the higher basicity and poorer π-acceptor capacity of pyridine, compared with pyrazine,[7] which in terms of the electroneutrality principle would tend to favour the lower co-ordination number. This would parallel our earlier observations on tetrahedral–octahedral equilibria which indicated that, in solution at least, the presence of iodide as ligand in cobalt(II) complexes stabilises the tetrahedral state.[2] In fact, qualitative estimates of the degree of dissociation (mainly into tetrahedral species) of NiL_4X_2 in chloroform showed that the ease of dissociation falls in the sequence $NCS \ll Cl < Br < I$, which is precisely that found for the corresponding cobalt(II) complexes.

The spectra of the mononuclear octahedral NiL_4X_2 complexes indicate that the ligand field is tetragonal, the tetragonality increasing from Cl to Br to I. While this is not surprising in view of the known positions of the three halide ions, relative to pyridine (or its derivatives) in the spectrochemical series,[10] it is interesting that the tetragonality is apparently not so serious in the corresponding bridged octahedral NiL_2X_2 complexes. In these the ligand field is effectively NiL_2X_4, and it might be expected that the ligand field should be similarly non-uniform since the same pairs of ligand partners are involved. A possible explanation, one that follows from the conclusions of Part I [2] is that in the mononulcear NiL_4X_2 compounds there is a greater degree of (*a*) charge transfer from X to Ni, and (*b*) back donation of electrons from Ni to L, than in the polymeric type of complex. This would have the effect of increasing the in-plane field (taking the halide ions to be axially placed) and thereby enhancing the ligand field asymmetry. In the NiL_2X_2 complexes, on the other hand, it seems unlikely that the halide ions, since they are bridging two metals ions, can promote $M \longrightarrow L$ π-bonding so effectively in which case a more uniform perturbation of the metal *d* orbitals will result.

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* Except where otherwise stated we use the terms tetrahedral and octahedral to include also distorted structures derived from them.

In principle at least, one way of testing these ideas would be to compare the electronic spectra of NiL_4X_2 complexes, where L = pyridine, with those in which for example L = NH_3, which cannot accept back co-ordinated electrons. In fact this is impossible since $Ni(NH_3)_4(Hal)_2$ complexes do not appear to exist;[14] instead, ionic complexes $[Ni(NH_3)_6][Hal]_2$ are formed in which the halide ions are not co-ordinated.[11,14] However, the apparent instability of $Ni(NH_3)_4(Hal)_2$ is itself, we suggest, an argument in favour of metal–pyridine π-bonding in the pyridine series since in this way an excessive accumulation of negative charge on the metal is avoided. In contrast, the non-ionic octahedral complex $Ni(NH_3)_4(NCS)_2$ is readily prepared.[16] We believe the stability of this compound to be due to a π-acceptor capacity on the part of the NCS ion which renders unnecessary any back-co-ordination to the neutral ligand in order to achieve electroneutrality. The bisammines $Ni(NH_3)_2Cl_2$ and $Ni(NH_3)_2Br_2$ are known, however, and their diffuse reflectance spectra are very similar to those of the corresponding aromatic amine complexes (Table **3**). These observations support the idea that in complexes containing bridging halogen the metal–halogen bond is less covalent.

Table **3** shows that, with one exception to be considered below, the spectral bands, ν_2 and ν_3, for the $NiLX_2$ group of complexes are intermediate in energy between those of the corresponding NiL_2X_2 and the NiX_2 compounds. In the former series the environment of each metal atom is made up by four X and two L ligands; in NiX_2 all six ligands are X ions and *Dq* falls as a consequence of the lower position of X, compared to L, in the spectrochemical series. The intermediate position of the spectral bands of $NipyCl_2$ has been considered by Sharp and his co-workers[15] as indicative of an octahedral ligand field comprising five chlorine ions and one nitrogen atom, and two possible polymeric structural arrangements were suggested. It is probable that all the compounds of this stoicheiometry reported here have similar structures. However, the red complex Ni(β-pic)Br_2 is exceptional in that the spectral bands occur at considerably lower frequencies than for the other monoamine bromides (see Table 3 and Figure 2). [The same is true, to a smaller extent, of the ν_2 band of the complex Ni(β-pic)$_2Br_2$]. This suggests a weaker average ligand field and, possibly also, variations in the Racah parameter. While it is not understood why β-picoline complexes should be different in this respect, we are inclined to the view that electronic rather than steric factors are responsible since there is no obvious steric explanation that does not equally well apply to other complexes of the same stoicheiometry.

EXPERIMENTAL

Preparation of NiL_4X_2 *Complexes* (X = Cl, Br, *or* I).—A hot ethanolic solution of the hydrated nickel(II) halide (1 mole) was added dropwise with stirring to a hot ethanolic solution of the appropriate amine (~4·5 mole). The crystalline product which settled out on cooling was filtered off, washed with cold ethanol containing a little amine, followed by a little cold chloroform, and dried in air. Recrystallisation was from ethanol containing ~5% amine.

X = NCS. Ethanolic solutions of hydrate nickel(II) nitrate (1 mole) and potassium isothiocyanate (2 moles) were mixed and the precipitated potassium nitrate filtered. The solution was evaporated to smaller bulk under an infrared lamp and filtered again directly into a hot ethanolic solution of the appropriate amine (~4·1 mole). The crystalline products slowly separated and were isolated and purified as described above.

NiL_2X_2 *Complexes*: $Nipy_2Cl_2$, $Nipy_2Br_2$, *or* Ni(β-pic)$_2Cl_2$.—Prepared as for the tetrakisamine complexes except that 1·8 moles of the appropriate amine were used. All were stored in a desiccator.

Ni(γ-pic)$_2Cl_2$. Ni(γ-pic)$_4Cl_2$ was gently refluxed in benzene for 30 min., the solution filtered while still hot, and the residue washed with hot benzene. The product was air dried at 60° and stored in a desiccator.

Ni(β-pic)$_2Br_2$ *or* Ni(γ-pic)$_2Br_2$. The corresponding tetrapicoline complexes were gently refluxed in xylene for 30 min. The yellow products separated out from the hot blue-violet solution. The mother-liquor was decanted off and the treatment repeated twice with fresh xylene. The products were dried at 60° and stored in a desiccator.

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[16] M. A. Porai-Kojie and L. M. Dicareva, *Kristallografiya*, 1959, **4**, 650.

$Ni(\gamma\text{-pic})_2I_2$. Di-iodotetra($\gamma$-picoline)nickel(II) was heated ***in vacuo*** at 80° for 4 hr. The dark green product was very hygroscopic and was stored in a desiccator.

$NiLX_2$ *complexes*. These were prepared by heating the corresponding tetrakisamine complexes in an oven at 140—150° for about 6 hr. They are hygroscopic and were stored in a desiccator.

Each of the complexes was analysed for nickel by EDTA titration in ammonia–ammonium chloride buffer solution at ~30°, murexide indicator being used. Observed analyses for the products used in the experiments described agreed with the theoretical values to ±0·1%.

The spectral, conductometric, and magnetic measurements were carried out as described previously.[2] Diamagnetic corrections were applied in each case.

The thermogravimetric experiments were carried out in air in a thermobalance of local design over the temperature range 20—400°. The same heating rate programme was used in all cases.

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

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