Infrared Spectra, Electronic Spectra, and Magnetic Properties of Dihalogenobis(pyrazine) Complexes of Cobalt(II) and Nickel(II): a Structural Re-assignment

By M. Goldstein,* F. B. Taylor, and W. D. Unsworth, Department of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB

Detailed studies have been made of the i.r. (to 80 cm^{-1}) and Raman spectra, and variable-temperature magnetic susceptibilities, of the complexes $MX_2(pyrazine)_2$ [M = Co or Ni; X = Cl, Br, or I]. It is shown that the compounds are of sheet structure, having metal atoms linked by pyrazine bridges, with *trans*-terminal halogen atoms, rather than the halogen-bridged chain structure previously proposed. This has necessitated a re-interpretation of their electronic spectra.

PREVIOUS studies [1] of the electronic spectra and room-temperature magnetic moments of complexes $MX_2(pyz)_2$ (M = Co or Ni; X = Cl, Br, or I; pyz = pyrazine) have shown that in these compounds the metal atoms are octahedrally co-ordinated. This co-ordination may be achieved either by bridging of halogen atoms, leaving the pyrazine groups unidentate, structure (I), or by bridging of the pyrazine ligands with terminal halogen, structure (II). On the basis of a mid-i.r. spectral criterion for the denticity of pyrazine,[1] structure (I), analogous to that found [2] for α-$CoCl_2(pyridine)_2$, was preferred.

We have recently investigated the i.r. and Raman spectra of some pyrazine complexes and have been able to characterise the vibrational spectral properties of unidentate and bidentate pyrazine groups more rigorously.[3] This work cast some doubt on the previously suggested [1] structure (I) of the $MX_2(pyz)_2$ compounds.

These latter systems are frequently referred to as 'model' compounds for discussion of electronic and

[1] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1962, 1235; 1963, 5042; 1964, 4761.
[2] J. D. Dunitz, *Acta Cryst.*, 1957, **10**, 307.
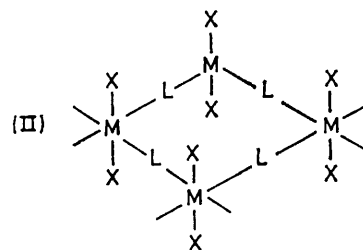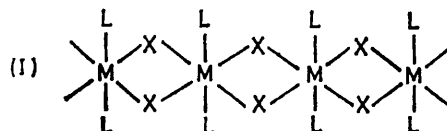
[3] M. Goldstein and W. D. Unsworth, *Spectrochim. Acta*, 1971, **27A**, 1055.

TABLE 1

Experimental and calculated magnetic data [a]

NiCl₂(py)₂

T/K	303·2	274·2	244·5	216·7	186·1	156·9	127·8	88·4
$10^6\chi_A$ (obs)	4604	5106	5817	6700	7907	9599	12,155	18,928
$10^6\chi_A$ (calc)	4691	5206	5874	6683	7889	9546	12,093	18,945
$\mu_{\rm eff}$/B.M.	3·26	3·27	3·31	3·35	3·38	3·43	3·49	3·64

NiBr₂(py)₂

T/K	303·2	274·2	244·5	216·7	186·1	156·9	127·8	88·4
$10^6\chi_A$ (obs)	4940	5442	6119	7056	8275	10,011	12,572	19,031
$10^6\chi_A$ (calc)	4976	5510	6198	7027	8255	9925	12,455	19,082
$\mu_{\rm eff}$/B.M.	3·38	3·38	3·40	3·44	3·46	3·51	3·55	3·65

NiCl₂(pyz)₂

T/K	333·2	303·2	274·2	244·5	216·7	186·1	156·9	127·8	88·4
$10^6\chi_A$ (obs)	3745	4090	4495	5023	5723	6621	7840	9587	13,742
$10^6\chi_A$ (calc)	3781	4134	4549	5076	5702	6608	7806	9550	13,770
$\mu_{\rm eff}$/B.M.	3·06	3·06	3·06	3·06	3·09	3·08	3·09	3·10	3·09

NiBr₂(pyz)₂

T/K	333·2	303·2	274·2	244·5	216·7	186·1	156·9	127·8	88·4
$10^6\chi_A$ (obs)	3681	4020	4417	4940	5613	6486	7668	9362	13,298
$10^6\chi_A$ (calc)	3725	4070	4475	4989	5598	6477	7634	9309	13,321
$\mu_{\rm eff}$/B.M.	3·03	3·03	3·03	3·03	3·06	3·05	3·06	3·06	3·04

NiI₂(pyz)₂

T/K	333·2	303·2	274·2	244·5	216·7	186·1	156·9	127·8	88·4
$10^6\chi_A$ (obs)	3443	3753	4119	4611	5208	6035	7122	8683	12,336
$10^6\chi_A$ (calc)	3469	3788	4163	4638	5201	6014	7084	8631	12,332
$\mu_{\rm eff}$/B.M.	2·93	2·93	2·92	2·93	2·93	2·93	2·94	2·94	2·93

[a] χ_A in c.g.s.u. $\mu_{\rm eff} = 2\cdot83\,[\chi_A \text{ (obs) } T]^{\frac{1}{2}}$.

TABLE 2

Mid-i.r. and Raman spectra (cm⁻¹) of $CoX_2(pyz)_2$ and related compounds [a,b]

CoCl₂(pyz)₂ Raman	CoCl₂(pyz)₂ I.r.	CoBr₂(pyz)₂ Raman	CoBr₂(pyz)₂ I.r.	CoI₂(pyz)₂ Raman	CoI₂(pyz)₂ I.r.	CoX₂(pyz) Raman	CoX₂(pyz) I.r.	Ag(NO₃)(pyz) Raman	Ag(NO₃)(pyz) I.r.
	3100sh		3115m		3110w		3110 ± 10mw		3100⎫
	3080m		3090m		3090m		3048 ± 8mw		3090⎬s
									3040⎭
3092s		3087m		3076s		3108w [e]		3084s	
								3070m	
1604s		1606w		1602s		1608w [e]		1604m	
1524m				1520m				1522m	
	1480m		1490m		1495w		1487 ± 3ms		1500s
	1405m		1410s		1420s		1418 ± 3s		1440s
1214s		1220m		1224s		1218 ± 6mw		1240m	
	1150s		1155⎫1150⎭s		1160s		1165 ± 5s		1155s
	1110s		1117s		1120s		1120s		1135s
			1090w		1090w		1090w [f]		1080s
	1050s		1055s		1060s		1056 ± 4s		1055s
1032vs		1030s		1028s		1034 ± 2ms		1028s	
	985s		990m		983s			980w	990w
918w				908m				920w	
	815⎫810⎭s		820⎫815⎭s		820s		788 ± 2s		820⎫800⎭s
750w		755wbr		764m		764 ± 4s		745m	
700s		700m		700s		704 ± 4s		700s	
650s		648m		648vs		649 ± 3s		672m	
	470s		473s		472s		474 ± 2s		437s

[a] I.r. data on NiX₂(pyz)₂ compounds are essentially similar to the Co analogues, but satisfactory Raman data were not obtained.
[b] Assignments for free pyz, SnX₄(pyz)₂ (X = Cl or Br), and SnX₄(pyz) (X = Cl, Br, or I) are given in ref. 3. [c] Ranges for X = Cl, Br, and I. [d] Bands due to nitrate groups at 1392w, 1344m, and 1044s (Raman); and at 1350s,br and 820s (i.r.). [e] X = Cl only.
[f] X = Cl and Br only.

vibrational spectra of other complexes;[4] it therefore became important to investigate their structures in more detail, and to review their spectral and magnetic properties in the light of the results. Since this investigation was completed, a single-crystal X-ray diffraction study on $CoCl_2(pyz)_2$ has been undertaken in this Department, and has confirmed the conclusions here deduced.[5]

EXPERIMENTAL

The complexes were prepared as previously described,[1] and their purity established by elemental analysis.

Mid-i.r. spectra of mulls in Nujol and hexachlorobutadiene were recorded on Perkin-Elmer models 237 (4000—650 cm⁻¹) and 137KBr (800—400 cm⁻¹) spectrometers. R.I.I.C. FS-520 (450—80 cm⁻¹) and FS-720 (200—20 cm⁻¹) interferometers were used to obtain the far-i.r. spectra (polyethylene or wax discs), the latter instrument at the P.C.M.U., Harwell. Raman spectra were obtained on a Cary model 81 spectrometer using He–Ne 632·8 nm laser excitation.

Magnetic susceptibilities (Table 1) were determined by the Gouy method over the temperature range 330—90 K, and were independent of field strength (5440, 6360, 7050 Oe) at each temperature studied.

RESULTS AND DISCUSSION

Mid-i.r. and Raman Spectra (4000—400 cm⁻¹).—Table 2 summarises the results for the $MX_2(pyz)_2$ compounds studied. The absence of coincidence between Raman and i.r. bands clearly indicates that in these systems the pyrazine ligands are centrosymmetrically co-ordinated. Furthermore, the i.r. and Raman activities of the modes are essentially the same as those found for known pyrazine-bridged complexes $SnX_4(pyz)$ (X = Cl, Br, or I),[3] $CoX_2(pyz)$ (X = Cl, Br, or I),[6] and $Ag(NO_3)(pyz)$ [7] (*cf.* Table 2), but markedly different to those of $SnX_4(pyz)_2$ (X = Cl or Br) [3] in which pyz is unidentate. In view of the octahedral co-ordination of the metal atoms,[1] the halogen atoms must be in terminal positions. A number of geometrical arrangements may be suggested on this basis, of which the regular sheet structure (II) is the most symmetrical.

Far-i.r. Spectra (400—80 cm⁻¹).—Results are given in Table 3, with representative spectra shown in the Figure. $CoX_2(pyz)_2$ (X = Cl or Br) were also studied to 20 cm⁻¹. It is immediately clear that the spectra of these complexes are very different to those known to have halogen-bridged octahedral structures as in (I) [*cf.* Figures 1 and 2 of ref. 6]. Moreover, comparison of chlorides, bromides, and iodides leads to the assignment

of only one ν(MN) and one ν(MX) band, whereas for complexes having $[MX_2]_n$ chains, two ν(MX) modes are predicted and found.[6]

For the octahedral polymeric sheet structure (II), the

TABLE 3

Far-i.r. spectra (cm⁻¹) of $MX_2(pyz)_2$ compounds

Complex	Temp.ᵃ	ν(MX) a_{2u}	ν(MN) e_u	δ(NMN) a_{2u} and e_u		δ(NMX) e_u
$CoCl_2(pyz)_2$	RTᵇ	260s	235s	162s	135s	125s
	LT	262s	245s	165s	137s	125s
$CoBr_2(pyz)_2$	RTᶜ	203s	232s	157s	{136s, 130sh}	105vs
	LT	207s	244s	157s	{137s, 130sh}	107vs
$CoI_2(pyz)_2$	RT	177s	228s	157mw	{138s, 130sh}	92s
	LT	182s	240s	160m	142s	92s
$NiCl_2(pyz)_2$	RT	260sh	250s	177s	140sbrᵈ	140sbrᵈ
	LT	262sᵈ	262sᵈ	147s		137s
$NiBr_2(pyz)_2$	RT	220s	246s	165s	146m	112vs
	LT	222s	257s	165s	147m	112vs
$NiI_2(pyz)_2$	RT	197s	242s	136s		96s
	LT	204s	252s	140s		98s

ᵃ RT = Room temperature, LT = *ca.* 100 K. ᵇ Studied to 20 cm⁻¹; additional band observed at 67 m. ᶜ Studied to 20 cm⁻¹; additional band observed at 52 m. ᵈ Coincident bands.
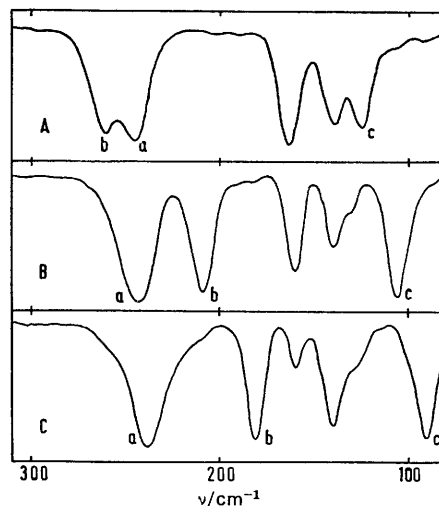
Far-i.r. spectra at *ca.* 100 K of A, $CoCl_2(pyz)_2$; B, $CoBr_2(pyz)_2$; C, $CoI_2(pyz)_2$; spectra of Ni analogues are similar; assignments (see Table 2): a, ν(CoN); b, ν(CoX); c, δ(NCoX)

following predictions for skeletal modes are made (pyz groups taken as point masses; sheet factor group D_{4h}):

$$\Gamma^{sheet} = a_{1g}(R) + e_g(R) + 2a_{2u} \text{ (i.r.)} + b_{2u} \text{ (inactive)} + 3e_u \text{ (i.r.)};$$

$$\Gamma_{MX}{}^{sheet} = a_{1g}(R) + a_{2u} \text{ (i.r.)};$$

$$\Gamma_{MN}{}^{sheet} = e_u \text{ (i.r.)}.$$

Hence only one ν(MX) and one ν(MN) band are predicted for the i.r. spectra, as are found.

Preliminary crystallographic studies show that

[4] See, *e.g.*, H. D. Stidham and J. A. Chandler, *J. Inorg. Nuclear Chem.*, 1965, **27**, 397; R. A. Walton, *J. Chem. Soc. (A)*, 1967, 1485; 1969, 61; M. Brierley and W. J. Geary, *J. Chem. Soc. (A)*, 1967, 963; R. W. Stotz, J. A. Walmsley, and F. Walmsley, *Inorg. Chem.*, 1969, **8**, 807; R. W. Matthews and R. A. Walton, *ibid.*, 1971, **10**, 1433; G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.*, 1964, 4330; B. E. Bridgland, G. W. A. Fowles, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 383; A. E. Allen, K. Feenan, and G. W. A. Fowles, *J. Chem. Soc.*, 1965, 1636; I. S. Ahuja and P. Rastogi, *J. Chem. Soc. (A)*, 1970, 2161.

[5] P. M. Carreck and E. M. McPartlin, personal communication.
[6] M. Goldstein and W. D. Unsworth, *Inorg. Chim. Acta*, 1970, **4**, 342.
[7] R. G. Vranka and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1020.

$CoCl_2(pyz)_2$ crystallizes in space-group $I4/mmm(D_{4h}^{17})$ with one formula unit per primitive cell.[5] Thus factor-group analysis of the crystal is identical with the sheet-group analysis. Hence five skeletal modes are predicted to occur in the i.r., in agreement with the number of i.r. bands observed in the region expected for these modes (350—80 cm^{-1}). These predictions are similar to those for Me_2SnF_2 and SnF_4.[8] If, as is likely, the pyrazine groups are oriented in the same way as the pyridine ligands in $MX_2(pyridine)_4$ [X = Cl, M = Co or Ni;[9] X = Br, M = Ni[10]], viz. propellor-like, then the factor group will be lower than D_{4h}. As a result, some new features may be observed, and indeed weak shoulders on the main bands are found.

It is clear that the spectra obtained are in very good agreement with the predictions made for structure (II), and (contrary to a recent report[11]) are inconsistent with a halide-bridged structure (I).

Magnetic Properties.—As the structure previously suggested[1] for the bis(pyrazine) complexes, (I), is analogous to that of corresponding bis(pyridine) compounds $MX_2(py)_2$,[2,12] it was necessary to compare the magnetic properties of both series. The nickel(II) compounds were chosen for study [$NiI_2(py)_2$ was excluded as it is a tetrahedral monomer[13]] because a d^8 ion in an octahedral field gives rise to an orbital singlet ground-state ($^3A_{2g}$) and the susceptibility of such a system can readily be fitted to that calculated for a particular model. The magnetic properties of $NiX_2(py)_2$ (X = Cl or Br) have been previously measured over a range of temperatures,[14] and our results are essentially similar. However, no attempt was made in the earlier work to fit the data to any particular model. Magnetic moments, at ambient temperature only, have previously been given for the $MX_2(pyz)_2$ compounds.[1]

TABLE 4

Magnetic parameters

	g	J/cm^{-1}	θ_4/K	10^2R ^{a}
$NiCl_2(py)_2$	2·23 ^{b} 2·22 ^{c}	+6·6	+22	0·60
$NiBr_2(py)_2$	2·33 ^{b} 2·30 ^{c}	+4·7	+20	0·64
$NiCl_2(pyz)_2$	2·17 ^{b} 2·16 ^{c}	+0·4	+2	0·51
$NiBr_2(pyz)_2$	2·16 ^{b} 2·13 ^{c}	−0·2	+2	0·57
$NiI_2(pyz)_2$	2·08 ^{b} 2·05 ^{c}	−0·3	+4	0·48

^{a} $R^2 = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi^2_{obs}]$. ^{b} From computer-fitting. ^{c} From plot of χ^{-1} against T.

All the $NiX_2(py)_2$ and $NiX_2(pyz)_2$ complexes studied show Curie–Weiss behaviour over the temperature range used; values of θ [$\chi \propto (T - \theta)^{-1}$] are given in Table 4.

The susceptibilities have been calculated for a linear system of ten atoms using a dipolar coupling model which includes in the perturbing Hamiltonian the term $-2\Sigma J_{ij}S_iS_j$, where J_{ij} is the isotropic exchange integral between the i-th and j-th centres of spin states S_i and S_j.[15] The use of a ten-atom model for polymeric systems is valid, because the susceptibilities of linear systems containing more than approximately four atoms have been shown to be similar over the present temperature range.[16] Calculations have also been made using the model of Fisher.[17] In both cases, the magnetic parameters (g and J) were varied until the best fits between the calculated and experimental susceptibilities were obtained. The temperature independent contribution to the susceptibility was taken as 230×10^{-6} c.g.s.u. As expected, the agreement between the results from the two models was very good over the temperature range used.

Theory predicts[18] a ferromagnetic interaction (θ and J positive) between two d^8 ions in octahedral sites when the angle between the bonds bridging the metal atoms (angle M–L–M) is 90°. The value of the exchange integral J should depend on the nature of the bridging group L, and decrease with decreasing M–M distance. For the halogen-bridged pyridine complexes (isomorphous[12] with α-$CoCl_2(py)_2$ in which the Co–Cl–Co angle is[2] 94·5°), this is exactly the behaviour observed (Table 4).

In contrast, the bis(pyrazine) complexes are apparently magnetically dilute (θ and J negligible). Moreover, the value of J is independent of halogen within experimental error (Table 4). It is clear, therefore, that the magnetic properties are inconsistent with the presence of $[NiX_2]_n$ halogen-bridged chains as in structure (I). In the proposed structure (II), the nickel–(bridging ligand)–nickel angle is 180°, in which case an antiferromagnetic interaction is predicted.[18] The apparent magnetic dilution in these compounds therefore suggests a counterbalancing ferromagnetic effect, which could arise either from the orthogonal overlap of pyrazine π-orbitals with nickel e_g orbitals, or from interaction between nickel atoms at opposite corners of the square arrays.

We conclude that the vibrational spectral and magnetic data are incompatible with a halogen-bridged structure (I) and are entirely consistent with the sheet arrangement (II). In view of this, it is pertinent to re-examine other data on these compounds, as follows.

Electronic Spectra.—In a previous analysis of the electronic spectra of $MX_2(pyz)_2$ compounds,[1] comparison was made with the spectra of corresponding X-bridged

[8] M. Goldstein and W. D. Unsworth, *J. Chem. Soc. (A)*, 1971, 2121.

[9] M. A. Porai-Koshits, *Trudy Inst. Kristallogr. Akad. Nauk S.S.S.R.*, 1954, **10**, 117.

[10] A. S. Antsishkina and M. A. Porai-Koshits, *Soviet Phys. Cryst.*, 1958, **3**, 684.

[11] J. R. Ferraro, J. Zipper, and W. Wozniak, *Appl. Spectroscopy*, 1969, **23**, 160.

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

[13] J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1966, 1031.

[14] D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 1964, 5194.

[15] J. H. Van Vleck, ' Theory of Electric and Magnetic Susceptibilities,' Oxford University Press, London, 1932.

[16] A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc. (A)*, 1966, 1656.

[17] M. E. Fisher, *Amer. J. Phys.*, 1964, **32**, 343; J. C. Bonner and M. E. Fisher, *Phys. Rev.*, 1964, *A*, **135**, 640.

[18] J. Kanamori, *J. Phys. and Chem. Solids*, 1959, **10**, 87.

$MX_2(py)_2$ series. This led to the conclusion that the crystal-field splitting energy of pyrazine was greater than

TABLE 5

Diffuse reflectance electronic spectra of six-co-ordinate complexes of nickel(II) halides with pyrazine or pyridine

Complex	Ref.	$\nu_{max}/(cm^{-1} \times 10^{-3})$				
$NiCl_2(pyz)_2$	1	10·5	12·2	16·15		
$NiCl_2(py)_4$	a	10·8	13·0	16·1	19·6	25·6
$NiCl_2(pyz)$	6	8·77		14·3		27·0
$NiCl_2(py)_2$	a		13·0	14·1	22·7	24·4
$NiBr_2(pyz)_2$	1	10·4		15·75		
$NiBr_2(py)_4$	a	10·5	12·5	15·4		25·0
$NiBr_2(pyz)$	6	8·7		14·3		
$NiBr_2(py)_2$	a			13·5		23·3
$NiI_2(pyz)_2$	1	10·6		15·6		
$NiI_2(py)_4$	a		12·3	15·8		25·0
$NiI_2(pyz)$	6	8·1				

a J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, J. Inorg. Nuclear Chem., 1964, 26, 1895; 1965, 27, 1529.

that of pyridine, and was explained in terms of greater π-bonding of the metal atom with the former ligand.[1]

However, since the present results show that the $MX_2(pyz)_2$ series are not X-bridged, a more appropriate comparison is with spectra of corresponding trans-$MX_2(py)_4$ complexes. This leads (e.g. Table 5) to the more reasonable conclusion that (bridging) pyrazine and (terminal) pyridine occupy essentially the same positions in the spectrochemical series. The close similarity between spectra of corresponding $MX_2(py)_2$ (X-bridged) and $MX_2(pyz)$ (X- and pyz-bridged) complexes (Table 5) supports this view. There is no evidence to suggest that π-bonding involving pyrazine is more significant than in pyridine complexes. In fact, since pyrazine is a weaker base towards the proton than pyridine [19] by a factor of ca. 10^4, back π-bonding from the metal is more likely than in the pyridine complexes.

19 C. R. Noller, ' Chemistry of Organic Compounds,' 3rd edn., Saunders, London, 1965, p. 690.