Far-infrared Spectra of Bis(pyrazine) Complexes of Transition Metal(II) Halides. The Crystal and Molecular Structure of Dichlorobis(pyrazine)cobalt(II)

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Summary Single crystal *X*-ray diffraction studies on $CoCl_2(pyrazine)_2$ confirm far-i.r. spectroscopic evidence that in $MX_2(pyrazine)_2$ [M = Co or Ni; X = Cl, Br, or I] the halogen atoms occupy terminal positions whereas the pyrazine groups are bridging, forming a sheet structure containing six-co-ordinate cobalt atoms.

BIS(PYRAZINE) complexes of cobalt(II) and nickel(II) halides, $MX_2(pyz)_2$, contain octahedrally co-ordinated metal atoms, as is evident from their electronic spectra and magnetic properties.[1] The presence of a band in the i.r. spectra at *ca.* 980 cm^{-1} [absent from the spectra of $(CuI)_2(pyz)$ and $(BCl_3)_2(pyz)$] was used as a basis for suggesting that the pyrazine groups were unidentate,[1] implying a halogen-bridged structure analogous to that[2] of α-$CoCl_2(pyridine)_2$. However, this mid-i.r. criterion has recently been shown to be erroneous.[3]

In the course of our studies on the vibrational spectra of octahedrally co-ordinated transition metal(II) complexes,[4] it became apparent that, contrary to a recent suggestion,[5] the far-i.r. spectra of $MX_2(pyz)_2$ compounds (M = Co or Ni; X = Cl, Br, or I) were not consistent with the presence of $[MX_2]_n$ chains. In each case a single $\nu(MX)$ mode was observed, rather than the two bands predicted and found for corresponding $[MX_2(pyridine)_2]_n$ and $[MX_2(pyz)]_n$ compounds.[4] Further, these $\nu(MX)$ bands (Table) occur *ca.* 40—80 cm^{-1} higher than in the halide-bridged systems. These observations are consistent with the presence of linear non-bridging X–M–X groupings. Moreover, we find that there are no coincidences between Raman and i.r. bands arising from internal vibrations of the pyrazine

TABLE

Metal–halogen stretching modes (cm^{-1}) *of* $MX_2(pyz)_2$ *complexes*

X = Cl		X = Br		X = I	
Co	Ni	Co	Ni	Co	Ni
260s	260s	203s	220s	177s	197s

ligands, implying (centrosymmetric) bidentate co-ordination of these groups.

In analysis of the electronic spectra of transition metal complexes such as of heteroaromatic amines, reference is frequently made to the hitherto supposed halogen-bridged structure of these $MX_2(pyz)_2$ compounds. Similarly, the existing far-i.r. data[5] might be cited as typical of halide-bridged structures. It was therefore of some importance to verify our interpretation of the vibrational data by carrying out a complete single-crystal *X*-ray examination. $CoCl_2(pyz)_2$ was chosen for study, since data on α-$CoCl_2(pyridine)_2$ [2] and $CoCl_2(pyridine)_4$ [6] are available for comparison.

Crystals of $CoCl_2(C_4N_2H_4)_2$ are tetragonal with $a = 7{\cdot}12$ and $c = 10{\cdot}63$ Å; D_m 1·77 g cm^{-3}, D_c 1·79 g cm^{-3} for $Z = 2$. The structure has been solved in space group *I*4/*mmm* which requires the cobalt atoms to be on sites of 4/*mmm* symmetry (0,0,0 and 0·5,0·5,0·5). The intensities of 138 independent reflections (Cu-K_α radiation) were estimated visually and anisotropic least-squares refinement has given $R = 0{\cdot}083$.

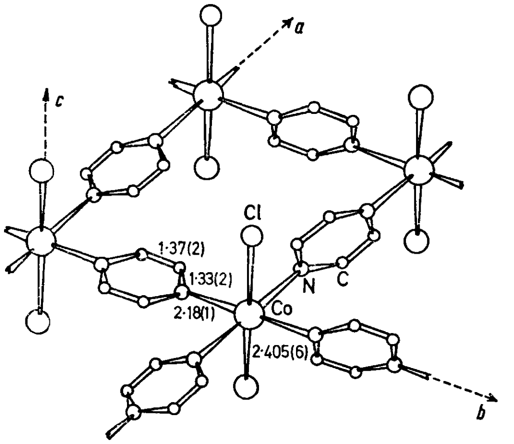

FIGURE. *Part of the sheet structure of dichlorobis(pyrazine)-cobalt*(II). *Bond lengths are in* Å *with e.s.d.'s in parentheses.*

The structure is made up of parallel sheets each consisting of an infinite square array of cobalt atoms bridged by bidentate pyrazine groups (Figure). The sheets alternate so that the Co atoms in one sheet lie vertically above and below the centres of the squares formed by the cobalt atoms of the adjacent sheets. Two chlorine atoms complete the octahedral configuration of each cobalt atom. The pyrazine rings are tilted about the N–N axes at an angle of 44·4° to the planes of the cobalt atoms, so that there are two orientations possible for each pyrazine ring depending on the direction of tilt. Calculations of hydrogen atom contacts between rings show that the four pyrazine molecules around a given cobalt atom must be arranged like propellor blades with identical orientation round all the cobalt atoms of one sheet. However, it is possible to have either right- or left-handed propellor screws. There are no steric factors which would prevent different propellor orientations occurring in adjacent sheets. Similar propellor orientations in all the sheets, or any systematic alternation of orientation between the sheets, may be ruled out because such arrangements would lead to repeat units in the *a* and *b* directions twice as great as those actually observed. The size of the tetragonal unit cell can be explained by a random distribution of the two possible propellor orientations between the sheets.

The structure was therefore refined in space group *I*4/*mmm* with half atom contributions from both orientations of the pyrazine ring.

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