Superexchange in Linear-chain 2,5-Dimethylpyrazinebis(pentane-2,4-dionato)-cobalt(II) and -nickel(II) Complexes

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The complexes [M(pd)$_2$(2,5Me$_2$-pyz)] (pd = MeCOCHOCMe; 2,5Me$_2$-pyz = 2,5-dimethylpyrazine; M = Co, Ni, or Cu) have been prepared and their powder magnetic susceptibilities measured between 1.7 and 70 K. The cobalt and nickel complexes are isomorphous, and all the three complexes probably consist of M(pd)$_2$ units linked axially into infinite chains by bridging 2,5Me$_2$-pyz molecules. The susceptibilities are analysed in terms of an exchange interaction $-2J\mathbf{S}_i \cdot \mathbf{S}_j$ between nearest neighbours within the chains, and good fits to the data are obtained with $4S^2J = -1.8 \pm 0.2, -1.7 \pm 0.1$, and 0 ± 0.1 cm^{-1} for M = Co, Ni, and Cu, respectively. The significance of these values in relation to the superexchange path through 2,5Me$_2$-pyz is briefly discussed.

IT is now well established that pyrazine can act as a bridging ligand,[1-5] and recent magnetic studies of linear-chain complexes of copper(II) have shown that, in spite of the length of the superexchange path, pyrazine can support significant spin–spin interaction between the

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metal ions.[6-10] In most cases where the presence of exchange has been inferred, the data can be satisfactorily reproduced by assuming a one-dimensional interaction of Heisenberg ($-2J\mathbf{S}_i \cdot \mathbf{S}_j$) type, and some selected results are listed in the Table.

Exchange parameters for the one-dimensional Heisenberg interaction $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$ in some pyrazine-bridged chain complexes

Complex	Ligand L	$-4S^2J$/cm^{-1}	Ref.
[Cu(NO$_3$)$_2$L]	pyz [a]	3.7 ± 0.05	7, 8
	Me-pyz	3.2 ± 0.1	10
	2,5Me$_2$-pyz	3.5 ± 0.1	10
[Cu(hfpd)$_2$L]	pyz [a]	0.0	9
[Cu(pd)$_2$L]	2,5Me$_2$-py	0.0 ± 0.1	*b*
[Ni(pd)$_2$L]	2,5Me$_2$-py	1.7 ± 0.1	*b*
[Co(pd)$_2$L]	2,5Me$_2$-py	1.8 ± 0.2	*b*

[a] The presence of · · · Cu–L–Cu–L · · · chains was confirmed by crystal-structure analyses. [b] This work.

The nature of the superexchange path through pyrazine (pyz) is of interest.[11] In [Cu(NO$_3$)$_2$(pyz)] the co-ordination is approximately square-planar CuO$_2$N$_2$ (the remaining two O atoms being weakly co-ordinated),[2] so that the spin-containing metal *d* orbital ($d_{x^2-y^2}$) must overlap strongly with the nitrogen lone pair. Because the plane of the pyz ring is at *ca.* 50° to the co-ordination plane, the $d_{x^2-y^2}$ orbital also has a small but non-zero overlap with the highest-occupied molecular orbital of the pyrazine π system, and hence both σ and π superexchange paths appear possible, although spectroscopic evidence suggests that the π path is the more important.[10] In [Cu(hfpd)$_2$(pyz)] (hfpd = F$_3$CCOCHCOCF$_3$) the co-ordination is tetragonal with long Cu–N bonds, the pyz ring lying approximately in the *xz* plane of the CuO$_4$N$_2$ system.[5] The unpaired electron is again likely to be mainly in the $d_{x^2-y^2}$ orbital, and the apparent absence of exchange in this case is in agreement with the lack of both σ and π paths for direct delocalisation of spin into ligand orbitals.

More information about the superexchange path through pyz might be obtained by introducing spin into other metal *d* orbitals and studying the effect of this on the exchange. We have therefore prepared the three complexes [M(pd)$_2$(2,5-Me$_2$-pyz)] (pd = MeCOCHOCMe, 2,5Me$_2$-pyz = 2,5-dimethylpyrazine; M = Co, Ni, or Cu), and we report the results of magnetic-susceptibility measurements between 1.7 and 70 K. Our attempts to prepare an analogous complex of manganese were unsuccessful.

EXPERIMENTAL

[M(pd)$_2$(2,5Me$_2$-pyz)] (M = Co *or* Ni).—2,5-Dimethylpyrazine (0.16 g, 1.48 mmol) in acetone (15 cm^3) was added dropwise over 5 min to a rapidly stirred solution of [M(pd)$_2$]·2H$_2$O (0.42 g, 1.43 mmol) in acetone (30 cm^3). The precipitate of minute needles (orange cobalt complex, pale green nickel) was filtered off, washed with acetone, and allowed to dry in air (Found: C, 52.45; H, 5.90; N, 7.60. Calc. for C$_{16}$H$_{22}$CoN$_2$O$_4$: C, 52.6; H, 6.05; N, 7.65. Found: C, 52.6; H, 6.30; N, 7.60. Calc. for C$_{16}$H$_{22}$N$_2$NiO$_4$: C, 52.65; H, 6.10; N, 7.70%). The complexes are insoluble in non-destructive solvents. Somewhat larger crystals can be obtained by exposing a dilute benzene solution of [M(pd)$_2$] to 2,5Me$_2$-pyz vapour in a desiccator for several hours. *X*-Ray powder photographs indicated that the two complexes are isomorphous; no lines due to [M(pd)$_2$]·2H$_2$O were visible.

2,5-Dimethylpyrazinebis(pentane-2,4-dionato)copper(II).—The complex [Cu(pd)$_2$] is insoluble in acetone and only sparingly soluble in cold 2,5-Me$_2$-pyz. After a few hours contact with 2,5Me$_2$-pyz at room temperature, however, the dull blue needles of [Cu(pd)$_2$] were converted into small turquoise-blue crystals {Found: Cu, 16.4. Calc. for [Cu(pd)$_2$(2,5-Me$_2$-pyz)(OH$_2$)]: Cu, 16.4%}. These reverted to [Cu(pd)$_2$] after a few minutes exposure to the atmosphere. The complex [Cu(pd)$_2$] dissolved in boiling 2,5Me$_2$-pyz to give a brown solution which on cooling deposited sea-green needles of [Cu(pd)$_2$(2,5Me$_2$-pyz)] (Found: C, 51.9; H, 5.95; Cu, 17.25; N, 7.55. Calc. for C$_{16}$H$_{22}$CuN$_2$O$_4$: C, 51.95; H, 6.00; Cu, 17.2; N, 7.60%). These also reverted to [Cu(pd)$_2$] after a few hours in air or in contact with a solvent. E.s.r. measurements at 9.5 GHz on a freshly prepared sample indicated $g_{\parallel} = 2.31$, $g_{\perp} = 2.08$, and $g_{\text{av.}} = 2.16 \pm 0.01$.

Attempted Preparation of Manganese Complex.—The complex [Mn(pd)$_2$]·2H$_2$O [12] in acetone or ethanol gave no precipitate with 2,5Me$_2$-pyz. This is consistent with the observation [12] that the complex gives stable adducts with pyridine and 4-methylpyridine but not with 2-methylpyridine.

Physical Measurements.—Reflectance spectra were recorded at room temperature against a magnesium oxide standard on a Unicam SP 700 instrument equipped with a SP 735 diffuse-reflectance attachment, and e.s.r. spectra on a Varian E3 spectrometer. Magnetic susceptibilities of finely powdered samples were measured between 1.7 and 70 K on a Princeton Applied Research model 155 vibrating-sample magnetometer at a field of 800 A mm^{-1} (10^4 Oersted); the susceptibilities were reproducible within 1% for different measurements on the same sample, and were not significantly field dependent at 4.2 K. Corrections were applied for diamagnetic contributions of -1.3 mm^3 mol^{-1} and for assumed temperature-independent paramagnetic (t.i.p.) contributions of 1.25, 2.25, and 0.75 mm^3 mol^{-1} for Co^{2+}, Ni^{2+}, and Cu^{2+} respectively [$4\pi \times 10^3$ mm^3 mol^{-1} (S.I.) = 1 cm^3 mol^{-1} (c.g.s.)].

RESULTS AND INTERPRETATION

Structures of the Complexes.—The reflectance spectra of the cobalt and nickel complexes (Figure 1) are consistent with slightly distorted octahedral co-ordination. The spectrum of [Co(pd)$_2$(2,5Me$_2$-pyz)] can be satisfactorily interpreted in terms of the approximate assignments $^4T_{2g}$ at 9 500 and $^4T_{1g}(P)$ at 18 100 cm^{-1}, from which we estimate

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Δ *ca.* 10 600, B *ca.* 650, and $^4A_{2g}$ at 20 000 cm^{-1}, while that of [Ni(pd)$_2$(2,5Me$_2$-pyz)] gives Δ *ca.* 9 800 cm^{-1}. The spectra, stoicheiometry, and insolubility of the two complexes, and their magnetic properties (see below), are consistent with their formulation as linear-chain polymers with bridging 2,5Me$_2$-pyz molecules, and *X*-ray measurements show that both complexes have the same structure.

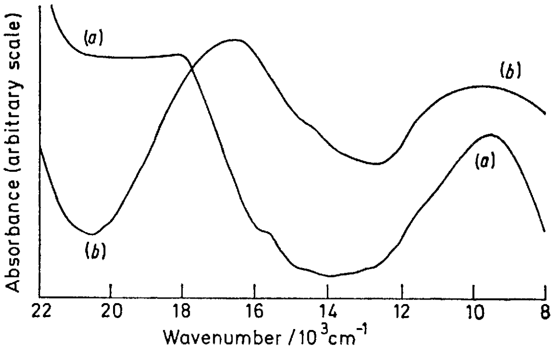

FIGURE 1 Reflectance spectra of [M(pd)$_2$(2,5Me$_2$-pyz)] [M = Co(*a*) or Ni(*b*)]

The copper complex is not isomorphous with the cobalt and nickel analogues, and also differs from them in its ready loss of 2,5Me$_2$-pyz and in its solubility in hot 2,5Me$_2$-pyz. It may be five-co-ordinate, but analogy with [Cu(hfpd)$_2$(pyz)],[5] and the somewhat greater stability of [Cu(pd)$_2$(2,5Me$_2$-pyz)] than [Cu(pd)$_2$(2,5Me$_2$-pyz)(OH$_2$)] against loss of 2,5Me$_2$-pyz, favour a linear-chain structure with rather weak axial bonds.

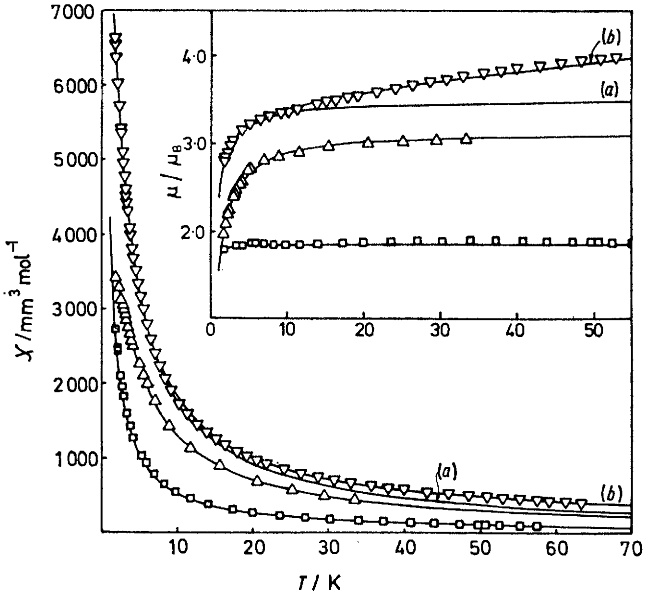

FIGURE 2 Magnetic susceptibilities and effective magnetic moments of [M(pd)$_2$(2,5Me$_2$-pyz)] [M = Co(▽), Ni(△), or Cu(□)], with curves calculated as described in the text

Magnetic Susceptibilities.—Figure 2 shows the experimental data, together with theoretical curves calculated as outlined below. The data have been deposited as Supplementary Publication No. SUP 22262 (5 pp.).* Theoretical parameters were determined by an unweighted least-squares fitting procedure minimising $\Sigma(\chi_{\text{obs.}} - \chi_{\text{calc.}})^2$, uncertainty limits being assigned by comparing the effects of small changes in the parameters with the estimated experimental uncertainty.

[Co(pd)$_2$(2,5Me$_2$-pyz)]. To interpret the magnetic behaviour of this complex we assume that the cubic-field $^4T_{1g}$ ground term of d^7 is split by spin–orbit coupling and by an axial component of the ligand field, corresponding to somewhat weaker bonding along the Co–N axis. (From the spectrum of the nickel analogue, and Reedijk's observation [13] that in several isomorphous tetragonal cobalt and nickel complexes the axial distortion splits the $^4T_{1g}(F)$ ground term of Co^{2+} by 30—40% of the splitting of the $^3T_{1g}(F)$ term of Ni^{2+}, we estimate that the axial splitting parameter D is probably only *ca.* 350 cm^{-1}, *i.e.* of the order of $2|\lambda|$, where λ is the spin–orbit coupling constant.) The effect of these perturbations is to split the $^4T_{1g}$ term into a number of degenerate levels, with a Kramers doublet lowest. At temperatures low enough that only the latter is occupied, the Hamiltonian $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$, representing isotropic exchange between adjacent real spins $S = \frac{3}{2}$, can be represented in terms of the pseudo-spin $S' = \frac{1}{2}$ of the ground doublet by the anisotropic spin Hamiltonian (1).

$$\mathscr{H} = -2J[\alpha S'_{1z}S'_{2z} + \beta(S'_{1x}S'_{2x} + S'_{1y}S'_{2y})] \qquad (1)$$

The constants α and β are related to the g values; in cubic symmetry $\alpha = \beta = \frac{25}{9}$ and $g = \frac{13}{3}$, while an axial distortion $D \gg |\lambda|$ gives $\alpha = g_{\parallel} = 9$ and $\beta = g_{\perp} = 0$. For small distortions, typical observed values are α and $g_{\parallel}$ *ca.* 5—7, β and $g_{\perp}$ *ca.* 1—3.[14,15]

Equation (1) is of Heisenberg form for $\alpha = \beta$ and tends towards Ising form as $\gamma = \beta/\alpha \rightarrow 0$. Bonner and Fisher [16] have shown that for γ *ca.* $\leqslant 0.3$ the Ising model should give a much better approximate description than the Heisenberg, and since an explicit treatment of the susceptibility problem for general γ has not yet been given, we chose to fit our data by using the one-dimensional Ising model for spin $\frac{1}{2}$, equations (2) and (3),[17] with $g_{\parallel}$, $g_{\perp}$, and $J' = \alpha J$ as

$$\chi_{\parallel} = \frac{Ng_{\parallel}^2\mu_B^2}{3kT} \cdot \frac{3}{4}\, e^{2x} \qquad (2)$$

$$\chi_{\perp} = \frac{Ng_{\perp}^2\mu_B^2}{3kT} \cdot \frac{3}{8}\,(x^{-1} \tanh x + \operatorname{sech}^2 x) \qquad (3)$$

parameters, and $x = J/2kT$. Because of the limitations of equation (1), only data for <15 K were used in the fitting procedure, which gave $g_{\parallel}$ *ca.* 5.8, $g_{\perp}$ *ca.* 2.8, and J' *ca.* -0.87 cm^{-1} [Figure 2(*a*)]. The g values imply α *ca.* 4.35, β *ca.* 1.45, hence J is -0.20 ± 0.02 cm^{-1}. The fit [measured by $R = (\Sigma\delta^2/\Sigma\chi^2)^{\frac{1}{2}}$] was good at <15 K (R 0.9%) but poorer over the whole temperature range (R 2.0%).

The experimental susceptibility values at >15 K are all higher than the calculated curve, the difference evidently being due to the upper components of $^4T_{1g}$, which we have neglected so far. Lines [18] has shown how the effect of these levels can be included approximately as an 'effective field' at higher temperatures. Because this model becomes

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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rather complicated when distortion is included, we have investigated its effects only on the assumption of cubic symmetry, which implies a Heisenberg-type interaction between the ground doublets. Since an explicit expression for the susceptibility of the Heisenberg chain is not available, we used the six-term series expansion of Rushbrooke and Wood,[19] (4), which should be fairly accurate above

$$\chi = \frac{Ng^2\mu_B^2}{3\boldsymbol{k}T} \cdot S(S+1)F_S(J,T) \qquad (4)$$

$$\text{where} \qquad F_S(J,T) = [1 + \sum_{n=1}^{6} b_n^{(S)}(J/\boldsymbol{k}T)^n]^{-1}$$

the Néel temperature. A fit of equation (4) ($b_n^{(\frac{1}{2})} = -1, 1, -\frac{1}{3}, \frac{1}{8}, \frac{29}{120}$, and $-\frac{317}{440}$ for $n = 1$—6) to the data at <15 K gave $g = 3.99$ and $\alpha J = -0.48$ cm^{-1}, which with $\alpha = \frac{25}{9}$ yields $J = -0.17 \pm 0.02$ cm^{-1} ($R = 1.0\%$ at <15 K, and 2.4% for all the data). The low g value can be attributed to orbital reduction, which can be shown to have the effect that the value $\frac{13}{3}$ for g should be replaced by $(10 + 3k)/3$, where $k(\leqslant 1)$ is an orbital-reduction factor.[*,14,20] Our result implies $k = 0.66$, which is a reasonable value. When Lines' correction is applied, g becomes a function of temperature, which can be calculated from the values of J', k, and λ. Using $J' = -0.48$, $\lambda = -180$ cm^{-1},[22] and $k = 0.63$ (so as to give g *ca.* 3.99 in the middle of the 0—10 K region) we obtain an excellent fit (R 1.2%) over the whole temperature range, as shown in Figure 2(*b*). The effectiveness of Lines' method in correcting for the neglect of upper levels is impressive; presumably a similar result would have been obtained if we had applied the correction to the more accurate Ising model for the ground-level interaction.

[Ni(pd)$_2$(2,5Me$_2$-pyz)]. From the spectroscopic value of Δ and assuming $\lambda = -270 \pm 20$ cm^{-1},[23] we estimate $g = 2.22 \pm 0.02$. The experimental susceptibility data deviate considerably from the Brillouin function [24] for a simple $S = 1$ paramagnet with g in this range, and inclusion of zero-field splitting of the $^3A_{2g}$ ground term (see the Appendix) affords little improvement and also requires an improbably large splitting ($g = 2.00$, $D = -9.7$ cm^{-1}, with $R = 7.4\%$). The data can, however, be satisfactorily interpreted in terms of a one-dimensional Heisenberg interaction, which we again describe by means of the Rushbrooke and Wood series expansion, equation (4) ($b_n^{(1)} = -\frac{8}{3}, \frac{44}{9}, -\frac{128}{27}, -\frac{4}{3}, \frac{11008}{1215}$, and $-\frac{5336}{3645}$ for $n =$ 1—6). The best fit over the whole temperature range (Figure 2) has $g = 2.22$, $J = -0.41 \pm 0.02$ cm^{-1}, and $R = 0.75\%$. At >5 K the data obey a Curie–Weiss law with $\chi^{-1} \propto (T/\text{K}) + 1.9$.

[Cu(pd)$_2$(2,5Me$_2$-pyz)]. The room-temperature e.s.r. spectrum shows an anisotropic signal with $g = 2.16 \pm 0.01$, and the susceptibility data give an almost exact fit to the Brillouin function [24] for a simple $S = \frac{1}{2}$ paramagnet with $g = 2.13$ and $R = 1.35\%$ (Figure 2). The Weiss constant is zero, and attempts to fit the data with equation (4) for a $S = \frac{1}{2}$ Heisenberg chain indicate that if such an interaction is present $|J| < 0.1$ cm^{-1}.

DISCUSSION

From the evidence discussed above, we assume that the cobalt and nickel complexes have a linear-chain structure consisting of planar M(pd)$_2$ groups linked axially by bridging dimethylpyrazine molecules. The structure of the copper complex is more uncertain, but its magnetic behaviour is similar to that of [Cu(hfpd)$_2$(pyz)], which is known to have a chain structure.[5]

In order to compare the strength of exchange in compounds having different numbers of unpaired electrons the J values must be multiplied by $4S^2$ to give the net effective exchange integrals.[25] The results for [M(pd)$_2$(2,5Me$_2$-pyz)] are -1.8 ± 0.2, -1.7 ± 0.1, and 0 ± 0.1 cm^{-1} for M = Co, Ni, and Cu, respectively. If we take the M–N direction as the z axis, and assume that the pyrazine ring plane is approximately parallel to one M–O bond (which we may take as the x axis), as in [Cu(hfpd)$_2$(pyz)],[5] the above results suggest that the d_{z^2} orbital is involved in exchange, presumably through the pyrazine σ-bond system, and that the $d_{x^2-y^2}$ and d_{xy} orbitals do not contribute significantly. It has been suggested that the effectiveness of pyrazine for mediating metal–metal interactions should be greatest when it operates through its σ system.[11] In the complexes [M(pd)$_2$(2,5Me$_2$-pyz)] the d_{xz} and d_{yz} orbitals probably contain little or no unpaired spin, so our results tell us nothing about the efficiency of any π paths that may exist. (In this connection it is unfortunate that we were unable to prepare an analogous manganese complex.) However, the considerably smaller magnitude of $4S^2J$ in the cobalt and nickel complexes compared with [Cu(NO$_3$)$_2$(pyz)] is in agreement with the view that a significant part of the interaction in the latter complex is due to superexchange through the pyrazine π system.

APPENDIX

For a $^3A_{2g}$ term with a zero-field spin Hamiltonian $D(S_z^2 - \frac{2}{3})$, the susceptibility, calculated to second order by standard methods [22,24] without approximation of the exponentials, is given by equations (5) and (6) where

$$\chi_{\parallel} = \frac{6x^{-1}\sinh x \exp(-y)}{1 + 2\cosh x \exp(-y)}\chi_0 \qquad (5)$$

$$\chi_{\perp} = \frac{6y^{-1}[1 - \exp(z)\exp(-y)]}{1 + 2\exp(z)\exp(-y)}\chi_0 \qquad (6)$$

$\chi_0 = Ng^2\mu_B^2/3\boldsymbol{k}T$, $x = g\mu_B H/\boldsymbol{k}T$, $y = D/\boldsymbol{k}T$, and $z = -3x^2/y$. The expression for $\chi_{\perp}$ is not valid if D is of the order of $g\mu_B H$ or smaller.

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[*] In this expression for g, used by Lines,[18] k includes both the orbital-reduction factor due to covalency effects and a factor $2A/3$, where A varies between 1.0 and 1.5, the strong- and weak-field limits respectively. The value of A calculated [21] from the spectrum of [Co(pd)$_2$(2,5Me$_2$-pyz)] is 1.36.

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