Structure, Spectroscopic and Angular-overlap Studies of Tris(pyrazol-1-yl)methane Complexes *

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The metal(II) complexes $[M\{(pz)_3CH\}_2][NO_3]_2$, where $(pz)_3CH$ is the symmetrical tripodal nitrogen-donor ligand tris(pyrazol-1-yl)methane, have been prepared for M = Co, Ni, Cu or Zn, and examined by single-crystal X-ray diffraction and electronic spectroscopy. The cations are centrosymmetric with the copper complex exhibiting a Jahn–Teller distortion. The ligand 'bite' angles N–M–N of 83.3(9)–86.2(1)° cause a slight trigonal distortion from octahedral geometry. The tripod ligand produces a relatively strong ligand field, consistent with the rather short metal–nitrogen bond lengths in the complexes. The pyrazole group acts as a moderately strong σ donor and a weak out-of-plane π donor, with the π interaction in the plane of the amine ligand probably being close to zero.

As discussed by Trofimenko,[1] tripod ligands containing nitrogen-donor heterocycles linked to a bridging carbon atom are used for a variety of applications in co-ordination and organometallic chemistry. Considerable interest has been shown in the relative importance of the electronic and steric characteristics of such ligands in influencing the oxidation state of the metal. For ligands like $(C_5H_4N)_3P$, C_5H_4N = pyridyl, it has been proposed[2] that low oxidation states may be stabilized by metal-to-ligand π bonding, this being facilitated by conjugation through the bridgehead atom. In a previous study[3] such features were investigated by determining the crystal structures and electronic spectra of first-row transition-metal complexes with the mixed-amine tripod ligand $(pz)_2(C_5H_4N)CH$, pz = pyrazolyl. It was found that the steric constraints of the ligand seem to be the major influence on the nature of the metal–ligand bonding. However, analysis of the crystal structures was complicated by disordering of the two amines, and the relatively complicated nature of the ligand meant that the π interaction in the plane of each amine had to be assumed to be negligible. For this reason it was decided to study the analogous complexes formed by the simpler ligand tris(pyrazolyl)methane $(pz)_3CH$. This ligand has been found to stabilize high-oxidation-state organopalladium(IV) complexes,[4] but little work on first-row transition-metal ions has been reported. The present study describes the crystal structures, spectral properties and metal–ligand angular-overlap bonding parameters of the bis complexes formed by the ligand with Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}.

Experimental

The ligand $(pz)_3CH$ was prepared as reported[4] and also purchased from Columbia Organic Chemicals, (Cassot, SC). The purity of the complexes was checked by microanalysis performed by the Central Science Laboratory, Hobart, Tasmania. Single-crystal and KBr disk electronic spectra were recorded using a Cary 17 spectrophotometer by a procedure described in detail elsewhere,[5] with the samples cooled using a Cryodyne model 22C cryostat. Absorption coefficients were estimated by measuring crystal thicknesses using a microscope with a graduated eyepiece. Room-temperature magnetic susceptibilities were measured using a Johnson Matthey magnetic susceptibility balance calibrated with $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$. The EPR spectra were recorded at room temperature on a JEOL JES-FE spectrometer operating at Q-band frequency, with the crystal rotated using the standard JEOL single-crystal accessory.

Synthesis of Metal(II) *Complexes* (M = Co, Ni, Cu *or* Zn).—A solution of the hydrated metal(II) nitrate in acetone was added slowly with stirring to a solution of $(pz)_3CH$ in acetone with a $M^{II}:(pz)_3CH$ mole ratio of 1:2. The precipitate formed was filtered off. In each case a yield of *ca.* 95% was obtained. The complexes were recrystallized by vapour diffusion of diethyl ether into a solution of the crude material in acetonitrile–methanol (1:2).

$[Co\{(pz)_3CH\}_2][NO_3]_2$: yellow crystals, μ_{eff} 4.7_7 (Found: C, 39.35; H, 3.35; N, 31.90. Calc. for $C_{20}H_{20}CoN_{14}O_6$: C, 39.30; H, 3.30; N, 32.10%).

$[Ni\{(pz)_3CH\}_2][NO_3]_2$: pink-purple crystals, μ_{eff} 2.9_4 (Found: C, 39.30; H, 3.25; N, 31.95. Calc. for $C_{20}H_{20}N_{14}NiO_6$: C, 39.35; H, 3.30: N, 32.10%).

$[Cu\{(pz)_3CH\}_2][NO_3]_2$: blue crystals, μ_{eff} 1.7_9 (Found: C, 39.95; H, 3.40; N, 32.10. Calc. for $C_{20}H_{20}CuN_{14}O_6$: C, 39.00; H, 3.40; N, 31.85%).

$[Zn\{(pz)_3CH\}_2][NO_3]_2$: colourless crystals (Found: C, 38.95; H, 3.30; N, 31.75. Calc. for $C_{20}H_{20}N_{14}O_6Zn$: C, 38.90; H, 3.25; N, 31.75%).

Crystallography.—Intensity data for each crystal were measured up to θ_{max} of 25.0° at room temperature on an Enraf-Nonius CAD4F diffractometer equipped with Mo-Kα radiation (graphite monochromator), λ = 0.7107 Å, employing the ω–2θ scan technique. The data sets were corrected for Lorentz and polarization effects and for the complexes of Co^{II} and Zn^{II} an analytical absorption correction was applied[6] but not for M = Ni^{II} owing to the spherical nature of the crystal. Crystal data are listed in Table 1.

The structures were solved from the interpretation of the respective Patterson synthesis and each refined by a full-matrix least-squares procedure based on *F*.[7] Non-H atoms were refined with anisotropic thermal parameters and H atoms, located from difference maps, were refined isotropically. A weighting scheme

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Crystal data for $[M\{(pz)_3CH\}_2][NO_3]_2$*

Compound	M = Co	M = Ni	M = Cu	M = Zn
Colour	Yellow	Pink	Blue	Colourless
Formula	$C_{20}H_{20}CoN_{14}O_6$	$C_{20}H_{20}N_{14}NiO_6$	$C_{20}H_{20}CuN_{14}O_6$	$C_{20}H_{20}N_{14}O_6Zn$
M	611.4	611.2	616.0	617.9
a/Å	9.937(1)	9.867(1)	9.983(1)	9.984(2)
b/Å	7.931(1)	7.888(1)	7.673(1)	7.962(1)
c/Å	17.109(2)	17.164(2)	17.082(2)	17.068(2)
β/°	102.18(1)	102.13(1)	101.53(1)	102.18(1)
U/Å^3	1318.0	1306.1	1282.1	1326.2
F(000)	622	624	626	628
D_c/g cm^{-3}	1.541	1.554	1.596	1.547
Crystal size/mm	0.56 × 0.31 × 0.22	0.30 diameter	0.08 × 0.08 × 0.09	0.50 × 0.34 × 0.39
μ/cm^{-1}	6.79	7.75	8.84	9.77
Max., min. transmission factors	0.882, 0.787		0.941, 0.912	0.686, 0.745
No. data measured	2764	3799	2544	2624
No. unique data	2330	2301	2248	2345
No. observed data $[I \geq 2.5\sigma(I)]$	1759	1903	1666	1772
R	0.040	0.037	0.028	0.035
k	1.16	3.51	1.00	1.90
g	0.0025	0.0003	0.0015	0.0006
R'	0.063	0.058	0.042	0.053
ρ/e Å^{-3}	0.60	0.65	0.27	0.49

* Details in common: monoclinic, space group $P2_1/n$; $Z = 2$.

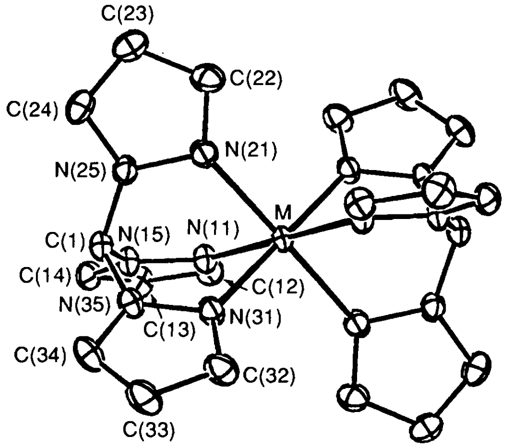

Fig. 1 Molecular structure and crystallographic numbering scheme for $[M\{(pz)_3CH\}_2][NO_3]_2$ [M = Co, Ni (illustrated), Cu or Zn]

of the form $w = k/[\sigma^2(F) + |g|F^2]$ was introduced for each structure and the refinements were continued until convergence; final refinement details are given in Table 1. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied in each case. Fractional atomic coordinates are listed in Table 2 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP[7] using 25% probability ellipsoids. Scattering factors for M^{II} (corrected for f' and f'') were from ref. 8 while those for the remaining atoms were those incorporated in SHELX 76.[6] Refinement was performed on a SUN4/280 workstation.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Special features. The four complexes are crystallographically isostructural and have the same stoichiometry $[M\{(pz)_3CH\}_2][NO_3]_2$ with a complex cation and unco-ordinated nitrate anions. All are unsolvated, and in every case the metal lies on a crystallographic inversion centre. The structures are essentially ordered, without the disorder found in complexes with $(pz)_2(C_5H_4N)CH$. However, the thermal parameters of the nitrate oxygen atoms in some of the structures are rather high, which may indicate some disorder, possibly dynamic.

Results and Discussion

Crystal Structures of the Complexes.—Important bond lengths and angles are listed in Table 3 and the stereochemistry of a typical complex, $[Ni\{(pz)_3CH\}_2]^{2+}$ is shown in Fig. 1. The bond lengths and angles of each pyrazole group are very similar, and exhibit the same pattern as that observed in complexes of pyrazole acting as a monodentate ligand. The structures of the complexes of Co, Ni and Zn are very similar; only the copper complex shows significant differences in the M–N bond lengths, presumably due to the Jahn–Teller effect. This distortion takes the normal, elongated tetragonal form, with two Cu–N bonds significantly longer than the other four. The magnitude of the Jahn–Teller distortion may be defined as $\rho = [2(\delta x^2 + \delta y^2 + \delta z^2]^{\frac{1}{2}}$ where δx, *etc.* represent the deviation of each bond length from the average value. The distortion in $[Cu\{(pz)_3CH\}_2]^{2+}$, ρ = 0.39 Å, is quite similar to that observed for the analogous complex $[Cu\{(pz)_2(C_5H_4N)CH\}_2][NO_3]_2$ (ρ = 0.42 Å) and for other complexes with nitrogen-donor ligands (*e.g.* ρ = 0.33 Å in $[Cu(tach)_2]^{2+}$ (tach = *cis,cis*-1,3,5-triaminocyclohexane[9]) and 0.36 Å in $[Cu(en)_3]SO_4$ (en = 1,2-diaminoethane[10]). Comparison of the average M–N bond lengths shows that these follow the sequence Zn > Cu ≈ Co > Ni expected from the ionic radii of the divalent metal ions.[11] However, they are significantly shorter than those in complexes involving monodentate pyrazole ligands, 2.072(2)–2.084(2) Å in the nickel complex, for instance, compared with ≈2.10 Å for monodentate pyrazole groups.[12] Similar metal–pyrazole bond lengths occur in $[M\{(pz)_2(C_5H_4N)CH\}_2][NO_3]_2$, where the Ni–N distances are 2.066(5) and 2.068(5) Å.[3] It seems likely that the relatively short bond lengths result from the steric constraints imposed by the tripodal nature of the ligands.

In every complex each pair of M–N bonds of the $(pz)_3CH$ ligand subtends a 'bite' angle of ≈84°, with the interligand N–M–N angles being ≈96°, resulting in a slight trigonal distortion from octahedral co-ordination geometry. The planes of the amine rings make angles of 40–41° with those defined by the M–N bond vectors, resulting in a 'paddle-wheel' conformation about the trigonal axis (Fig. 1). The 'bite' of each chelate ring and the geometry of the tripod ligand result in an unsymmetrical orientation of each amine ligand with respect to the M–N direction. For the complexes of Co, Ni and Zn the M–N–N angles are all between 116.7(2) and 117.5(2)° and the M–N–C angles are significantly larger, being between 136.7(2) and 138.0(2)°; for the copper(II) compound the distortion is even more pronounced for the two weakly bound ligands (Table 3).

Table 2 Fractional atomic coordinates for $[M\{(pz)_3CH\}_2][NO_3]_2$

Atom	*x*	*y*	*z*	*x*	*y*	*z*
(*a*) M = Co^{II}				(*b*) M = Ni^{II}		
M	0.5(−)	0.0(−)	0.0(−)	0.5(−)	0.0(−)	0.0(−)
N(11)	0.5264(3)	−0.1568(3)	0.1020(2)	0.5297(2)	−0.1536(3)	0.1005(1)
N(15)	0.4106(3)	−0.2054(3)	0.1269(2)	0.4155(2)	−0.2034(3)	0.1263(1)
N(21)	0.3581(3)	0.1302(3)	0.0536(2)	0.3609(2)	0.1315(3)	0.0525(1)
N(25)	0.2720(3)	0.0373(3)	0.0872(2)	0.2747(2)	0.0397(3)	0.0875(2)
N(31)	0.3334(3)	−0.1647(3)	−0.0451(2)	0.3359(2)	−0.1633(3)	−0.0442(1)
N(35)	0.2483(2)	−0.2051(3)	0.0045(2)	0.2504(2)	−0.2042(3)	0.0047(1)
C(1)	0.2781(3)	−0.1456(4)	0.0857(2)	0.2804(3)	−0.1434(3)	0.0857(2)
C(12)	0.6272(4)	−0.2462(5)	0.1463(2)	0.6333(3)	−0.2418(4)	0.1438(2)
C(13)	0.5772(5)	−0.3533(5)	0.1981(2)	0.5854(3)	−0.3497(4)	0.1967(2)
C(14)	0.4395(4)	−0.3251(5)	0.1839(2)	0.4457(3)	−0.3227(4)	0.1835(2)
C(22)	0.3259(4)	0.2894(5)	0.0664(3)	0.3304(3)	0.2921(4)	0.0644(2)
C(23)	0.2227(4)	0.2966(6)	0.1085(3)	0.2257(3)	0.3014(4)	0.1072(2)
C(24)	0.1880(4)	0.1357(5)	0.1204(2)	0.1907(3)	0.1394(4)	0.1199(2)
C(32)	0.2845(3)	−0.2463(5)	−0.1129(2)	0.2865(3)	−0.2440(4)	−0.1123(2)
C(33)	0.1672(4)	−0.3364(5)	−0.1070(3)	0.1681(3)	−0.3348(4)	−0.1065(2)
C(34)	0.1470(3)	−0.3100(4)	−0.0323(2)	0.1478(3)	−0.3079(3)	−0.0315(2)
N(100)	0.5175(3)	0.7888(4)	0.6979(2)	0.5202(2)	0.7882(3)	0.6993(2)
O(101)	0.4511(3)	0.8463(5)	0.7429(2)	0.4538(3)	0.8484(4)	0.7445(2)
O(102)	0.6020(4)	0.8710(4)	0.6748(3)	0.6054(3)	0.8692(3)	0.6752(3)
O(103)	0.4931(5)	0.6517(6)	0.6692(5)	0.4960(4)	0.6467(4)	0.6745(3)
(*c*) M = Cu^{II}				(*d*) M = Zn^{II}		
M	0.5(−)	0.0(−)	0.0(−)	0.5(−)	0.0(−)	0.0(−)
N(11)	0.5301(2)	−0.1481(3)	0.1004(1)	0.5248(3)	−0.1587(3)	0.1036(2)
N(15)	0.4182(2)	−0.2031(3)	0.1280(1)	0.4081(3)	−0.2057(3)	0.1273(2)
N(21)	0.3600(2)	0.1299(3)	0.0460(1)	0.3565(3)	0.1301(3)	0.0541(2)
N(25)	0.2770(2)	0.0398(3)	0.0853(1)	0.2704(3)	0.0365(3)	0.0869(2)
N(31)	0.3275(2)	−0.2086(3)	−0.0418(1)	0.3325(3)	−0.1666(3)	−0.0461(2)
N(35)	0.2438(2)	−0.2245(3)	0.0118(1)	0.2471(2)	−0.2059(3)	0.0035(2)
C(1)	0.2831(2)	−0.1474(3)	0.0899(1)	0.2769(3)	−0.1457(4)	0.0851(2)
C(12)	0.6345(3)	−0.2304(4)	0.1452(2)	0.6229(4)	−0.2493(5)	0.1481(2)
C(13)	0.5919(3)	−0.3378(4)	0.2005(2)	0.5704(5)	−0.3561(5)	0.1994(2)
C(14)	0.4545(3)	−0.3186(4)	0.1878(2)	0.4346(4)	−0.3253(5)	0.1842(2)
C(22)	0.3322(3)	0.2961(4)	0.0555(2)	0.3237(4)	0.2881(5)	0.0666(3)
C(23)	0.2323(3)	0.3134(4)	0.1010(2)	0.2193(4)	0.2939(6)	0.1086(3)
C(24)	0.1988(3)	0.1491(4)	0.1186(2)	0.1854(4)	0.1335(5)	0.1202(2)
C(32)	0.2604(3)	−0.2867(4)	−0.1073(2)	0.2822(4)	−0.2474(5)	−0.1134(2)
C(33)	0.1355(3)	−0.3490(4)	−0.0967(2)	0.1675(4)	−0.3372(5)	−0.1078(2)
C(34)	0.1271(3)	−0.3083(4)	−0.0201(2)	0.1478(3)	−0.3097(5)	−0.0328(2)
N(100)	0.5256(2)	0.7823(3)	0.7075(1)	0.5156(3)	0.7896(4)	0.6961(2)
O(101)	0.4528(3)	0.8271(4)	0.7535(2)	0.4490(3)	0.8440(5)	0.7415(2)
O(102)	0.6234(2)	0.8734(3)	0.6983(2)	0.5994(4)	0.8708(4)	0.6732(3)
O(103)	0.4990(3)	0.6502(4)	0.6666(2)	0.4911(6)	0.6526(6)	0.6675(4)

For a range of complexes involving monodentate pyrazole ligands the M–N–N angles are ≈125° and the M–N–C angles ≈129°.[12,13] This suggests that in the $[M\{(pz)_2(C_5H_4N)CH\}_2][NO_3]_2$ complexes the 'lone pair' orbital on the ligand nitrogen atom deviates by ≈8° from the M–N bond vector. It has been proposed[14] that deviations of this kind sometimes influence the bonding parameters of metal complexes, and this possibility is considered in a following section.

Electronic Spectra.—The electronic spectra of the cobalt, nickel and copper complexes were measured at 290 and 15 K, both for single crystals and as KBr discs. Typical spectra are shown in Figs. 2–4. The crystallographic symmetry of all four complexes is C_i, but the ligand co-ordination geometry about the metal ion in the compounds of Co and Ni closely approaches D_{3d} symmetry. The band intensities are quite low, being somewhat higher at 290 K, in agreement with the centrosymmetric nature of the complexes.

The spectrum of the nickel(II) complex consists of a highly asymmetric peak centred at ≈12 700 cm^{-1}, and a pair of bands at 18 100 and 20 800 cm^{-1}. These may be assigned to transitions to the $^3T_{2g}$ and $^3T_{1g}(F)$ levels of the parent octahedral complex, split by the trigonal distortion of the ligand field. In addition, weak, sharp peaks occur at 13 800 and 22 200 cm^{-1}, which may be assigned to spin-forbidden transitions. A shoulder at ≈27 000 cm^{-1} resolved in the mull spectrum [Fig. 2(*a*)] is most likely due to a charge transfer or intraligand transition, since the transition to the $^3T_{1g}(P)$ level is calculated to lie at considerably higher energy (≈30 500 cm^{-1}). In the D_{3d} point group the $^3T_{2g}$ state splits into $^3A_{1g}$ and ^3E_g, and $^3T_{1g}(F)$ into $^3A_{2g}$ and ^3E_g. The vibronic selection rules of the D_{3d} point group show that vibrations are available to induce intensity into transitions to each of the above states, so that the band polarizations cannot be used to aid their assignment, which therefore rest solely upon the calculations described below.

The spectrum of the cobalt(II) compound shows a highly asymmetric band centred at ≈12 000 cm^{-1}, which may be assigned to transitions to the $^4A_{1g}$ and ^4E_g states derived from the $^4T_{2g}$ level of the parent octahedral complex, a cluster of sharp peaks at ≈20 000 cm^{-1} which may be assigned to spin-forbidden transitions, and a broad, composite peak at ≈22 500 cm^{-1} which probably encompasses the transitions to the $^4A_{2g}$ and ^4E_g states from the $^4T_{1g}$ level and the transition to the $^4A_{2g}(P)$ state. It should be noted that the transition to the latter state normally gives rise to a very weak band,[15] so that its assignment is tentative.

Table 3 Selected bond distances (Å) and angles (°) for $[M\{(pz)_3CH\}_2][NO_3]_2$

	M					M			
	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}		Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}
M-N(11)	2.114(3)	2.077(2)	2.082(2)	2.145(3)	N(35)-C(1)	1.438(4)	1.441(3)	1.441(3)	1.443(4)
M-N(21)	2.108(3)	2.072(2)	2.001(2)	2.130(3)	N(15)-C(14)	1.348(4)	1.348(4)	1.347(3)	1.345(4)
M-N(31)	2.122(2)	2.084(2)	2.355(2)	2.150(2)	N(25)-C(24)	1.352(4)	1.345(4)	1.347(3)	1.358(4)
N(11)-N(15)	1.365(4)	1.352(3)	1.363(3)	1.364(3)	N(35)-C(34)	1.354(4)	1.348(3)	1.347(3)	1.339(4)
N(21)-N(25)	1.346(4)	1.350(3)	1.355(3)	1.345(4)	C(12)-C(13)	1.393(6)	1.398(5)	1.383(4)	1.400(6)
N(31)-N(35)	1.356(3)	1.349(3)	1.363(3)	1.358(3)	C(22)-C(23)	1.374(6)	1.390(5)	1.388(4)	1.384(5)
N(11)-C(12)	1.327(4)	1.327(4)	1.324(3)	1.319(4)	C(32)-C(33)	1.389(5)	1.392(4)	1.380(4)	1.370(5)
N(21)-C(22)	1.331(4)	1.327(4)	1.322(3)	1.329(4)	C(13)-C(14)	1.357(6)	1.366(5)	1.353(4)	1.348(6)
N(31)-C(32)	1.328(4)	1.330(3)	1.326(3)	1.320(4)	C(23)-C(24)	1.348(6)	1.353(5)	1.354(4)	1.346(6)
N(15)-C(1)	1.436(4)	1.448(3)	1.440(3)	1.437(4)	C(33)-C(34)	1.351(5)	1.359(5)	1.363(4)	1.354(5)
N(25)-C(1)	1.452(4)	1.446(3)	1.439(3)	1.453(4)					
N(11)-M-N(21)	84.6(1)	85.5(1)	86.8(1)	84.3(1)	N(35)-N(31)-C(32)	105.6(2)	105.7(2)	104.6(2)	104.9(3)
N(11)-M-N(31)	83.7(1)	84.6(1)	81.5(1)	83.3(1)	N(11)-N(15)-C(1)	119.9(2)	119.6(2)	120.7(2)	120.4(3)
N(11)-M-N(21′)	93.4(1)	94.5(1)	93.2(1)	95.7(1)	N(11)-N(15)-C(14)	111.1(3)	111.7(2)	110.6(2)	110.9(3)
N(11)-M-N(31′)	96.3(1)	95.4(1)	98.5(1)	96.7(1)	C(1)-N(15)-C(14)	128.5(3)	128.2(2)	128.6(2)	128.1(3)
N(21)-M-N(31)	85.2(1)	86.2(1)	86.1(1)	85.2(1)	N(21)-N(25)-C(1)	120.4(2)	119.7(2)	120.8(2)	120.6(3)
N(21)-M-N(31′)	94.8(1)	93.8(1)	93.9(1)	94.8(1)	N(21)-N(25)-C(24)	111.5(3)	111.8(2)	110.8(2)	111.7(3)
M-N(11)-N(15)	117.3(2)	117.3(2)	118.2(1)	116.7(2)	C(1)-N(25)-C(24)	128.1(3)	128.5(2)	128.3(2)	127.7(3)
M-N(11)-C(12)	137.2(2)	136.7(2)	136.3(2)	137.6(2)	N(31)-N(35)-C(1)	119.9(3)	119.6(2)	119.7(2)	119.8(2)
M-N(21)-N(25)	117.5(2)	117.5(2)	119.0(2)	117.3(2)	N(31)-N(35)-C(34)	110.8(3)	111.4(2)	111.6(2)	110.8(3)
M-N(21)-C(22)	137.9(2)	137.4(2)	135.1(2)	137.9(2)	C(1)-N(35)-C(34)	129.2(3)	129.0(2)	128.6(2)	129.3(3)
M-N(31)-N(35)	117.4(2)	117.4(2)	111.5(1)	117.1(2)	N(15)-C(1)-N(25)	111.0(3)	110.6(2)	110.3(2)	111.2(3)
M-N(31)-C(32)	137.0(2)	136.8(2)	141.1(2)	138.0(2)	N(15)-C(1)-N(35)	110.3(3)	109.7(2)	110.7(2)	110.7(3)
N(15)-N(11)-C(12)	104.8(3)	105.1(2)	104.9(2)	104.9(3)	N(25)-C(1)-N(35)	110.1(3)	110.6(2)	111.0(2)	110.6(3)
N(25)-N(21)-C(22)	104.7(3)	105.1(2)	105.5(2)	104.9(3)					

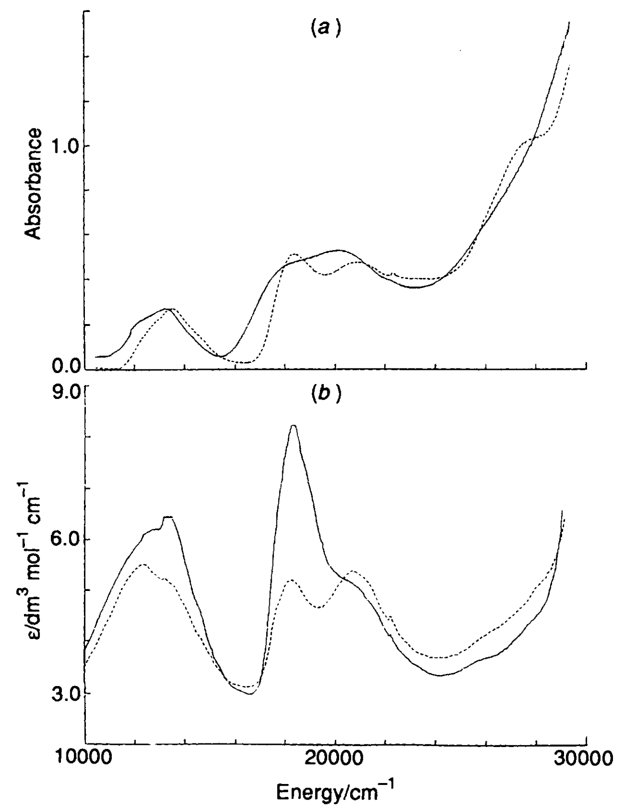

Fig. 2 Electronic spectrum of $[Ni\{(pz)_3CH\}_2][NO_3]_2$ recorded (*a*) as a KBr disk at room temperature (———) and ≈ 15 K (– – – –) and (*b*) as a single crystal at ≈ 15 K with the electric vector of the polarized light along each of the two extinction directions of an arbitrary crystal face

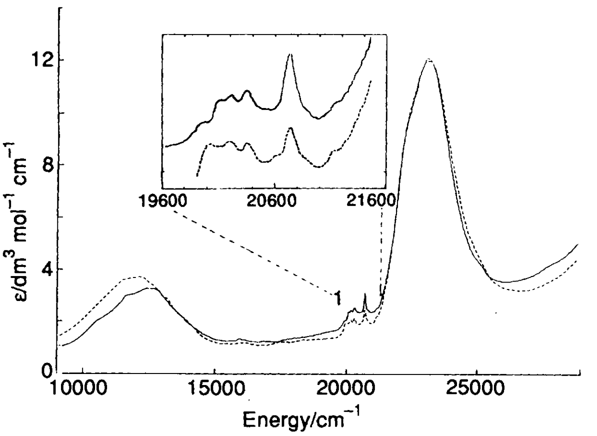

Fig. 3 Electronic spectrum at ≈ 15 K of a single crystal of $[Co\{(pz)_3CH\}_2][NO_3]_2$ with the electric vector of the polarized light along each of the two extinction directions of an arbitrary crystal face

The spectrum of the copper(II) compound consists of a band at 9800 cm^{-1}, a central peak occurring as a well resolved shoulder at 14 700 cm^{-1} and a peak at 17 000 cm^{-1} having a pronounced shoulder at ≈ 16 000 cm^{-1} in one polarization (Fig. 4). Though the symmetry of the complex $[Cu\{(pz)_3CH\}_2]^{2+}$ is no higher than C_i, the primary co-ordination sphere has approximate D_{4h} symmetry. In this point group the transition $^2B_{1g}(x^2 - y^2) \longrightarrow {}^2B_{2g}(xy)$ is forbidden in z polarization. However, the projection of the electric vector upon the z molecular axis is virtually identical for the two extinction directions of the well developed crystal face of the complex, (001), so that the band polarizations cannot be used to help assign the spectrum. For a tetragonally elongated complex of this type the excited electronic states are expected to follow the energy sequence $^2E_g(xz,yz) > {}^2B_{2g}(xy) > {}^2A_g(z^2)$, and the bands have been assigned in this manner, the splitting of the highest-energy peak being due to the deviation from strict tetragonal symmetry. The energies of the band maxima and their assignments are listed for each complex in Table 4.

EPR Spectrum of $[Cu\{(pz)_3CH\}_2]^{2+}$.—The EPR spectrum of a powder of $[Cu\{(pz)_3CH\}_2][NO_3]_2$ exhibits a well resolved EPR spectrum (Fig. 5) which yields $g_z = 2.250$, $g_{xy} = 2.061$,

Table 4 Metal–ligand bonding parameters, and calculated and observed transition energies of the complexes in cm^{-1}. See text for method of calculation

$[Ni\{(pz)_3CH\}_2][NO_3]_2$			$[Co\{(pz)_3CH\}_2][NO_3]_2$			$[Cu\{(pz)_3CH\}_2][NO_3]_2$		
Excited state	Obs.	Calc.	Excited state	Obs.	Calc.	Excited state	Obs.	Calc.
$^3A_{2g}$	12 200	12 300	$^4A_{1g}$	11 500	11 500	^2A_g	9 800	9 800
^3E_g	13 150	13 100	^4E_g	12 655	12 350	^2B_g	14 700	14 750
^1E_g	13 500	13 300	*	20 015	20 400	^2E_g	≈16 000	15 740
$^3A_{2g}$	18 100	18 000	*	20 230	20 600		17 000	17 000
^3E_g	20 800	20 700	*	20 655	20 700			
		20 950	$^4A_{2g}$	22 150	22 100			
$^1A_{1g}$	22 300	22 450	^4E_g	23 250	23 200			
Bonding parameters								
e_σ	4700, 4775, 4650			4550, 4675, 4400			5500, 5900, 800	
$e_{\pi y}$	630, 635, 615			585, 600, 575			775, 830, 250	
$e_{\pi x}$	0, 0, 0			0, 0, 0			0, 0, 0	
Racah parameters								
$B = 800, C = 3500$			$B = 845, C = 3500$			Obs.: $g_{xy} = 2.061, g_z = 2.250$ Calc.: $g_x = 2.051, g_y = 2.067, g_z = 2.252$		

* Spin-doublet state, the specific assignment of which is uncertain.[15]

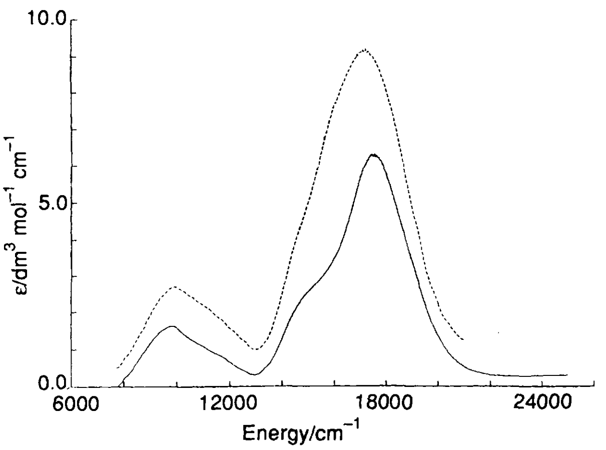

Fig. 4 Electronic spectrum at ≈15 K of a single crystal of $[Cu\{(pz)_3CH\}_2][NO_3]_2$ with the electric vector of the polarized light along each of the two extinction directions of an arbitrary crystal face

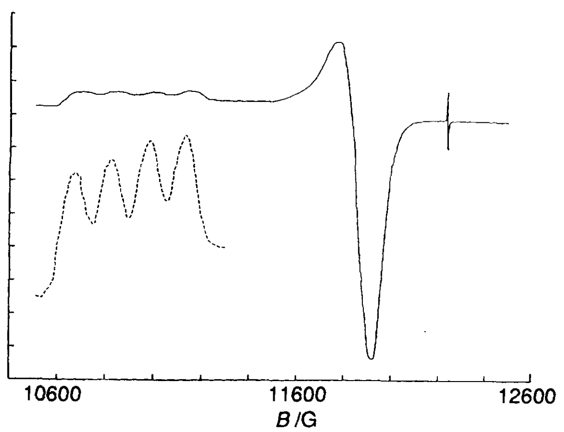

Fig. 5 The EPR spectrum of a powder of $[Cu\{(pz)_3CH\}_2][NO_3]_2$ recorded at Q-band frequency (≈34.2 GHz). The sharp resonance at ≈12 000 G (G = 10^{-4} T) is due to a speck of powdered dpph (diphenylpicrylhydrazyl) used as a reference (g = 2.0036). The region 10 500–11 300 G is shown with an expended intensity as an insert

and $|A_z| = 162 \times 10^{-4}$ cm^{-1}. It should be noted that these represent true molecular parameters, since signals due to both molecules in the unit cell were resolved in the EPR spectra of a single crystal of the compound.

The g shifts from the free-electron value are related to the excited-state energies by the perturbation expressions (1) and (2). Substitution of $\lambda = -828$ cm^{-1} for the value of the spin–orbit coupling constant, together with the excited-state energies listed in Table 4, yields the estimates $k_z = 0.74$, $k_{xy} = 0.76$ for the orbital reduction parameters. These values are similar to those derived for other amine complexes,[16] and although a quantitative interpretation is not warranted,[17] they imply a significant covalent contribution to the bonding in the complex. This is confirmed by the hyperfine splitting, which is related to the unpaired spin density α^2 in the ground-state wavefunction by the expressions (3) and (4). The isotropic Fermi parameter K has been estimated as 0.43, and the dipolar constant P as 0.036 cm^{-1},[18] and assuming the observed value of A_z to be negative yields the estimate $\alpha^2 = 0.72$. This lies towards the lower end of the range of estimates of α^2 = 0.71–0.78 made recently[19] for a range of copper(II) complexes. Substitution of the value α^2 = 0.72 in equation (4) yields the estimate $A_{xy} = -0.0021$, which is consistent with the fact that the in-plane hyperfine splitting of the compound is too small to be resolved (Fig. 5).

$$\delta g_z = -8\lambda k_z^2/E_{xy} \quad (1)$$

$$\delta g_{xy} = -2\lambda k_{xy}^2/E_{xz,yz} \quad (2)$$

$$A_z = P[-K\alpha^2 - (4\alpha^2/7) + (3\delta g_{xy}/7) + \delta g_z] \quad (3)$$

$$A_{xy} = P[-K\alpha^2 + (2\alpha^2/7) + (11\delta g_{xy}/14)] \quad (4)$$

Metal–Ligand Bonding Parameters.—The relatively high energies of the 'd–d' transitions indicate that the $(pz)_3CH$ tripod ligand produces a rather strong ligand field, considerably stronger than that in the corresponding complexes involving monodentate pyrazole groups. Thus, the lowest-energy transition of $[Ni(Hpz)_6]^{2+}$ occurs at 11 000 cm^{-1},[20] whereas that of $[Ni\{(pz)_3CH\}_2]^{2+}$ is at ≈12 700 cm^{-1}. A similarly high ligand field was observed for the mixed-amine tripod ligand $(pz)_2(C_5H_4N)CH$, and here it was inferred[3] that this was probably caused by the unusually short metal–ligand bond lengths induced by the steric constraints of the tripod ligand, rather than any π-acceptor character in the metal–ligand bonding.

To investigate the bonding characteristics of the present compounds, the computer package CAMMAG, developed by Gerloch and co-workers,[21] was used to estimate the metal–ligand bonding parameters of the complexes within the framework of the angular overlap model (a.o.m.).[22] This program calculates the transition energies of a complex, using as input the σ- and π-bonding parameters of the ligand donor atoms and the molecular geometry indicated by the crystal structure. In the present case, this involved the parameters e_σ, $e_{\pi x}$ and $e_{\pi y}$ for each pyrazole group, where $e_{\pi x}$ and $e_{\pi y}$ describe the π bonding parallel and perpendicular to the plane of the amine ring, respectively. It should be noted that in mixed-ligand complexes it is not possible to determine all the bonding parameters independently, and it has usually been assumed that the $e_{\pi x}$ parameter of ligands such as pyrazole is zero.[3,23] The present study provides an opportunity to test the validity of this assumption.

Initially the parameters found for monodentate pyrazole ligands, scaled as described previously[3] for the $[M(pz)_2(C_5H_4N)CH\}_2]^{2+}$ complexes to take into account the differences in bond lengths, were used to calculate the excited-state energies of the complexes of Ni^{II} and Co^{II}. Here, $e_{\pi x}$ was set equal to zero. Good agreement with experiment for $[Ni\{(pz)_3CH\}_2]^{2+}$ was obtained assuming Racah parameters B = 800 and C = 3500 cm^{-1}, with all transition energies less than 300 cm^{-1} from those observed experimentally (spin–orbit coupling was neglected in the calculations). The Racah parameters are reduced to ≈75% of their free-ion values,[24] this reduction agreeing well with the above analysis of the copper(II) EPR parameters. The sensitivity of the calculated transition energies to the bonding parameters was investigated, and it was found that increasing $e_{\pi x}$ invariably worsens agreement with experiment unless e_σ and $e_{\pi y}$ are increased by similar amounts. Thus, with a value of $e_{\pi x}$ = 500 cm^{-1} good agreement with experiment could only be obtained using $e_{\pi y}$ = ≈1130 cm^{-1} and e_σ = ≈5070 cm^{-1}. The most probable cause of a positive value of $e_{\pi x}$ is the rotation of the amine 'lone pair' orbital away from the metal–nitrogen bond vector. Such an effect has been inferred from an analysis of the optical spectra of several copper(II) acetylacetonato[25] and cobalt(II) Schiff-base[26] complexes, where it was described by the introduction of an additional a.o.m. parameter e_{pis}. However, in a conventional treatment, the presence of 'bent bonds' in the plane of the amine should cause both an effective change in $e_{\pi x}$ and a concomitant *decrease* in the e_σ parameter. It would thus appear that the relatively small rotation of the nitrogen 'lone pair' orbitals away from the metal–ligand bond axis in the $[Ni\{(pz)_3CH\}_2]^{2+}$ complex (≈8°) has no significant effect on the a.o.m. bonding parameters, and that the in-plane π bonding due to the amine is indeed negligible, as assumed in other studies.[23,27] Similar conclusions concerning the in-plane π interactions of heterocyclic amines have been drawn from several other studies.[23,28] Marginally better agreement with experiment could in fact be obtained using a small negative value for $e_{\pi x}$ = −100 cm^{-1}, but this difference from zero is not considered significant, and a negative value for the in-plane π-bonding interaction seems chemically unreasonable.

The use of bonding parameters only slightly smaller than those adopted for the nickel(II) complex also produced reasonable agreement with experiment for the cobalt complex, except for the transition to the $^4A_{2g}(P)$ state. However, the band due to the transition to the latter state is normally extremely weak,[15] so that it is reasonable that it is not resolved from the relatively intense peak assigned to the transition to the ^4E_g state which is only ≈1000 cm^{-1} lower in energy. Racah parameters B = 845 cm^{-1}, C = 3500 cm^{-1} were used for the cobalt(II) compound, the reduction from the free-ion values (≈85%)[24] implying that the bonding may be somewhat more ionic than that in the analogous nickel(II) and copper(II) complexes.

Transferral of the bonding parameters derived for the nickel(II) complex provided a good fit to the spectrum of the copper(II) complex, as far as the four closely bound ligands are concerned, after correcting for the differences in bond length (Table 4). However, the optimum value of e_σ for the weakly bound axial ligands (800 cm^{-1}) is significantly smaller than expected simply on the basis of the increase in bond lengths (≈2200 cm^{-1}). This discrepancy is most likely caused by configuration interaction between the metal $a_g(z^2)$ and $a_g(4s)$ orbitals.[29] Since the energy of the $a_g(z^2)$ orbital depends upon $2e_\sigma$, the above discrepancy implies a depression of ≈2800 cm^{-1} due to this configuration interaction. This seems reasonable, being about half the depression deduced for planar, four-coordinate copper(II) complexes, and very similar to that inferred for complexes having similar tetragonal distortions by Deeth and Gerloch.[30] As discussed above for the nickel(II) compound, it was found that the use of a non-zero value for $e_{\pi x}$ invariably produced a poorer fit with experiment, unless the other bonding parameters were also increased, which seems chemically unreasonable. The g values calculated using CAMMAG agree quite well with those observed experimentally (Table 4) assuming an isotropic orbital reduction parameter k = 0.78 which is comparable to the value of α^2 (= 0.72) derived from the copper(II) hyperfine splitting.

The bonding parameters derived for the $[M\{(pz)_3CH\}_2]^{2+}$ complexes are quite similar to those of the pyrazole groups in the analogous $[M\{(pz)_2(C_5H_4N)\}_2]^{2+}$ complexes.[3] They suggest that the $(pz)_3CH$ ligand is a rather strong σ donor and a moderate π donor. For the complexes of Ni^{II} and Co^{II} the ligand-field strength is significantly greater than that observed for pyrazole as a monodentate ligand. This is consistent with the short metal–ligand bond lengths associated with the tripod ligand. As observed in other studies,[23] the bonding parameters of the nickel(II) complex are somewhat larger than those of the cobalt(II) compound, while those of the tightly bound in-plane ligands in the copper(II) complex are higher still. The copper(II) parameters (e_σ = ≈5750 cm^{-1}, $e_{\pi y}$ = ≈800 cm^{-1}) agree well with those deduced[27] for planar complexes of substituted pyrazole ligands with this metal ion (e_σ = ≈6600, $e_{\pi y}$ = ≈1070 cm^{-1}) when the shorter Cu–N bond lengths in the latter are taken into consideration.

Conclusion

The large overall ligand-field splitting observed for each $[M\{(pz)_3CH\}_2]^{2+}$ complex is due to the relatively strong σ-donor and moderate π-donor capacity of the tripod ligand, this probably being caused by the relatively short M–N bonds in the compounds. Although the crystal structures suggest that the directions of the nitrogen 'lone pair' orbitals deviate somewhat from the M–N bond vectors, this does not appear to influence the metal–ligand bonding parameters. Optimum agreement between the calculated and observed transition energies of the complexes is obtained if the in-plane π interaction of the ligand is negligible.

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