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Distorted Trigonal Pyramidal Structure in a Cobalt(II) Complex with the Novel Ligand Tris(3,5-dimethyl-1-pyrazolylethyl)amine

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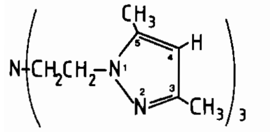
As part of a general research on the coordination chemistry of polydentate ligands containing pyrazole rings as donor groups [1], we synthesized the novel ligand tris(3,5-dimethyl-1-pyrazolylethyl)amine (I) hereafter indicated as MeTPyEA) and a number of 3d metal(II) complexes whose characterization is still in progress.



I

A cobalt complex having the formula [Co(MeTPyEA)]$(BPh_4)_2$ has been obtained from the reaction of any cobalt(II) halide and the ligand in the presence of $NaBPh_4$. Our interest has focussed first on this complex for its electronic spectrum with bands at *ca.* 0.7, 1.3, 1.7 and 2.1 μm^{-1} (Fig. 1) is rather similar to the spectra of five-coordinated trigonal bipyramidal complexes of cobalt(II) [2], whilst the potential donor atoms are at the most four. We have therefore performed an X-ray analysis of the [Co(MeTPyEA)]$(BPh_4)_2$ complex to find out its stereochemistry.

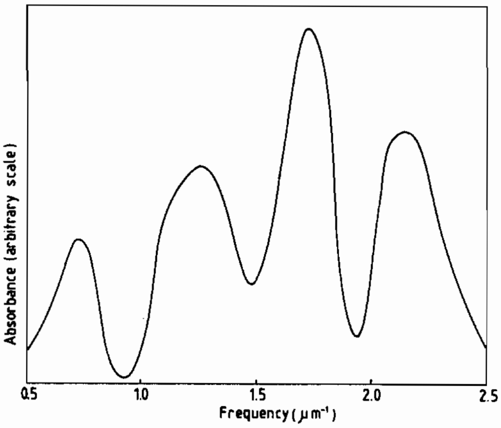


Fig. 1. Diffuse reflectance spectrum of [Co(MeTPyEA)]$(BPh_4)_2$.

Experimental

The ligand was prepared starting from $N(CH_2CH_2Cl)_3$ [3] and potassium 3,5-dimethylpyrazolate with a procedure similar to that already described for the synthesis of the ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine [4].

The [Co(MeTPyEA)]$(BPh_4)_2$ complex was prepared as follows: warm solutions of the ligand in absolute ethanol and $NaBPh_4$ in acetone were added in succession to a warm solution of a cobalt(II) halide in absolute ethanol. The resulting solution was concentrated and cooled to room temperature to effect crystallization. Recrystallization from absolute ethanol–acetone solution yields blue crystals suitable for X-ray diffraction.

The crystals are triclinic, spage group $P\bar{1}$, a = 16.977(5), b = 14.314(5), c = 12.629(4) Å, α = 81.09(7)°, β = 82.35(7)°, γ = 86.27(7)°. Two unit formulae $C_{69}H_{77}N_7B_2Co$ are present in the unit cell.

TABLE I. Atomic Parameters for Anisotropically Refined Atoms.[a]

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
Co	2225(1)	2073(1)	2515(1)	558(10)	462(10)	411(9)	−1(7)	−53(7)	6(7)
N1	1856(5)	2782(6)	1062(6)	743(61)	576(59)	361(56)	0(46)	−106(47)	−92(48)
N2	2630(5)	914(6)	1980(7)	469(61)	680(61)	551(59)	−39(49)	−165(50)	−26(50)
N3	2349(5)	593(6)	1137(7)	580(65)	533(65)	658(62)	53(51)	19(52)	−112(53)
N4	3030(5)	2925(6)	2709(7)	636(60)	632(57)	279(58)	−42(47)	−46(50)	−5(48)
N5	3436(6)	3458(7)	1850(8)	846(68)	752(66)	360(66)	−139(55)	−114(57)	−107(56)
N6	1236(5)	2124(6)	3488(7)	630(63)	606(62)	444(60)	57(48)	−80(50)	17(53)
N7	636(6)	2792(7)	3233(7)	672(70)	827(69)	476(66)	0(53)	−19(59)	−62(60)

[a] The Form of the Thermal Ellipsoid is $\exp[-2T^2(U11H^2A^{*2} + U22K^2B^{*2} + U33L^2C^{*2} + 2U12HKA^*B^* + 2U13HLA^*B^* + 2U23KLB^*C^*)]$; all quantities are multiplied by 10^4.

TABLE II. Atomic Parameters for Isotropically Refined Atoms.[a]

Atom	X	Y	Z	U (Å^2)
C1	1745(7)	1150(7)	607(9)	688(34)
C2	1961(7)	2164(7)	217(9)	638(32)
C3	2360(7)	3621(8)	683(10)	714(36)
C4	3227(7)	3449(9)	793(9)	729(35)
C5	993(7)	3092(8)	1259(9)	660(34)
C6	760(7)	3488(8)	2295(9)	714(35)
C7	3637(8)	370(9)	3203(10)	918(42)
C8	3198(7)	248(8)	2320(9)	657(33)
C9	3244(7)	−456(9)	1670(9)	725(36)
C10	2725(7)	−238(8)	947(9)	643(33)
C11	2481(8)	−770(10)	144(11)	933(43)
C12	3039(7)	2622(9)	4692(9)	739(36)
C13	3363(6)	3066(7)	3570(9)	568(31)
C14	3978(7)	3675(8)	3249(9)	717(35)
C15	3996(8)	3914(9)	2166(10)	747(36)
C16	4536(9)	4554(10)	1354(11)	1069(48)
C17	1441(7)	824(8)	4965(10)	833(38)
C18	951(7)	1620(8)	4441(9)	619(32)
C19	218(8)	1977(9)	4777(10)	838(39)
C20	36(8)	2700(9)	4035(10)	735(36)
C21	−720(9)	3351(11)	3997(13)	1195(54)
C22	4265(4)	3473(5)	7097(5)	563(30)
C23	4362(4)	3996(5)	6064(5)	741(34)
C24	4075(4)	4936(5)	5899(5)	850(40)
C25	3691(4)	5354(5)	6768(5)	891(41)
C26	3595(4)	4831(5)	7801(5)	846(39)
C27	3882(4)	3891(5)	7966(5)	745(34)
C28	5306(4)	2122(6)	6346(7)	548(30)
C29	5098(4)	1801(6)	5437(7)	937(42)
C30	5677(4)	1683(6)	4568(7)	1117(49)
C31	6464(4)	1887(6)	4608(7)	983(44)
C32	6672(4)	2208(6)	5517(7)	908(42)
C33	6093(4)	2326(6)	6386(7)	720(35)
C34	3818(4)	1648(5)	7367(6)	566(30)
C35	3986(4)	693(5)	7283(6)	838(40)
C36	3367(4)	95(5)	7296(6)	929(43)
C37	2581(4)	451(5)	7392(6)	800(38)
C38	2413(4)	1406(5)	7476(6)	644(33)
C39	3032(4)	2004(5)	7463(6)	532(30)
C40	4906(4)	2157(5)	8560(6)	553(30)
C41	5432(4)	2788(5)	8786(6)	714(35)
C42	5693(4)	2674(5)	9802(6)	909(41)
C43	5429(4)	1929(5)	10591(6)	925(43)
C44	4903(4)	1298(5)	10365(6)	882(41)
C45	4642(4)	1413(5)	9349(6)	692(34)
C46	−1310(3)	3753(5)	7373(6)	614(31)
C47	−938(3)	4423(5)	6574(6)	655(33)
C48	−1381(3)	4978(5)	5835(6)	828(39)
C49	−2196(3)	4863(5)	5896(6)	897(41)
C50	−2568(3)	4193(5)	6695(6)	955(43)
C51	−2125(3)	3639(5)	7434(6)	974(44)
C52	−621(4)	1953(6)	7882(6)	585(30)
C53	41(4)	1387(6)	8168(6)	717(34)
C54	148(4)	470(6)	7912(6)	968(43)
C55	−407(4)	119(6)	7370(6)	897(41)
C56	−1068(4)	685(6)	7085(6)	935(42)
C57	−1175(4)	1602(6)	7341(6)	697(35)
C58	125(4)	3564(5)	8119(5)	580(30)
C59	189(4)	4261(5)	8759(5)	567(30)
C60	874(4)	4779(5)	8604(5)	681(34)
C61	1494(4)	4601(5)	7810(5)	740(35)
C62	1431(4)	3904(5)	7170(5)	725(36)
C63	746(4)	3386(5)	7324(5)	683(34)
C64	−1185(4)	2935(5)	9518(7)	619(31)
C65	−834(4)	2275(5)	10267(7)	789(38)
C66	−1169(4)	2137(5)	11347(7)	975(44)
C67	−1855(4)	2660(5)	11677(7)	1004(45)
C68	−2206(4)	3321(5)	10927(7)	1088(48)
C69	−1872(4)	3458(5)	9848(7)	921(42)
B1	4583(7)	2332(8)	7335(9)	504(34)
B2	−783(8)	3051(9)	8245(10)	585(37)

[a] All quantities are multiplied by 10^4.

Intensity data were collected on a Phillips PW 1100 diffractometer and structure determination and refinement were carried out using 3181 observed reflections ($I \geqslant 3\sigma(I)$) up to a $2\theta \leqslant 40$. The SHELX system of programs was used for crystallographic computations. Full matrix least squares refinement in which the phenyl groups were treated as rigid bodies and hydrogen atoms introduced at calculated positions have a final conventional reliability factor of 0.079.

A list of observed and calculated structure factors can be obtained from the authors. The final atomic parameters are listed in Tables I and II.

Results and Discussion

The [Co(MeTPyEA)]$(BPh_4)_2$ derivative has a room temperature magnetic moment of 4.22 μ_B*, a value indicative of three unpaired electrons. The structure of the complex is comprised of [Co(MeTPyEA)]$^{2+}$ cations and BPh_4^- anions. A perspective drawing of the cation is given in Fig. 2 along with bond distances and angle values of importance.

An examination of the structural parameters shows that the coordination polyhedron about the cobalt can be described as a trigonal pyramid distorted toward a tetrahedron. In fact the three angles at the cobalt atom and including the N(1) atom, with values of about 100°, diverge from the ideal tetrahedron value of 109.5° toward the ideal 90° value of the apical angles in a trigonal pyramid. The remaining three angles, with an average value of 117.5° approach the 120° value of the equatorial angles

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*1 $\mu_B = 9.27 \times 10^{-24}$ A m^2.

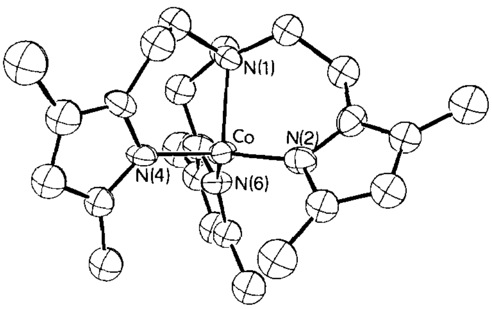

Fig. 2. Molecular structure of the [Co(meTPyEA)]$^{2+}$ cation. Bond lengths and angles of importance are: Co–N(1), 2.107(8); Co–N(2), 1.939(8); Co–N(4), 1.953(8); Co–N(6), 1.949(8) Å; N(1)–Co–N(2), 97.1(3)°; N(1)–Co–N(4), 99.7(3)°; N(1)–Co–N(6), 100.7(3)°; N(2)–Co–N(4), 115.6(3)°; N(2)–Co–N(6), 121.6(3)°; N(4)–Co–N(6), 115.3(3)°.

in the same ideal geometry. Even more significant is the distinction between a long apical Co–N distance of 2.107(8) Å and the three short equatorial Co–N distances of 1.947(8) Å (av.). Conversely, the displacement of the cobalt atom above the equatorial plane (0.31 Å) evidences the tetrahedral distortion of the complex.

An interesting question is why the cobalt does not pick up a fifth donor atom, *e.g.* a halide, at the empty position of a trigonal bipyramid. We suggest that the screening effect of bulky 3-methyl substituents at the pyrazole rings is of greatest importance. In fact one hydrogen atom of each methyl group is as close as 1.62 Å to the point of the trigonal bipyramid C_3 axis where an hypothetical halide ligand would be approximately located, *i.e.* 2.40 Å from the equatorial plane.

Finally, the lengthening of one cobalt–axial ligand bond distance has been previously observed in five-coordinated trigonal-bipyramidal complexes with little affect on the electronic spectra [5]. The results here reported indicate that this holds even in the limiting case of the complete removal of one axial ligand, provided that a distinction between in-plane and axial metal–ligand interactions can still be made. Such a distinction, on the contary, vanishes in the regular tetrahedral geometry.

References

1 P. Dapporto, F. Mani and C. Mealli, *Inorg. Chem., 17,* 1323 (1978); F. Mani, *Inorg. Chim. Acta, 38,* 97 (1980).
2 M. Ciampolini and N. Nardi, *Inorg. Chem., 5,* 41 (1966); M. Ciampolini and P. Paoletti, *Inorg. Chem., 6,* 1263 (1967).
3 W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc., 74,* 5822 (1952).
4 F. Mani and G. Scapacci, *Inorg. Chim. Acta, 38,* 151 (1980).
5 L. Sacconi and I. Bertini, *J. Am. Chem. Soc., 90,* 5443 (1968); J. L. Shafer and K. N. Raymond, *Inorg. Chem., 10,* 1799 (1971).