

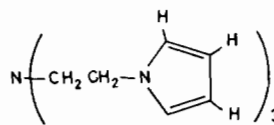
Transition Metal Complexes from Vanadium(II) to Copper(II) with the Tetradentate Ligand Tris(1-pyrazolyloethyl)amine

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Recently we synthesized the novel tetradentate ligand tris(3,5-dimethyl-1-pyrazolyloethyl)amine, MeTPyEA, and a number of complexes with most 3d metal(II) ions [1]. Some of these complexes have been found to have both structural and spectral properties quite uncommon [2]. Since transition metal complexes of polypyrazolyl ligands are growing in interest for their relevance as bioinorganic models [3], we have undertaken the synthesis of the less sterically hindered ligand tris(1-pyrazolyloethyl)amine (hereafter indicated as TPyEA) and of the metal complexes with a number of 3d metal(II) ions. The appearance of a paper dealing with copper(I) and copper(II) complexes with the same ligands MeTPyEA and TPyEA [4], prompted us to report preliminary physico-chemical properties of a few representative complexes amongst those obtained with the ligand TPyEA.



Experimental

The ligand TPyEA was prepared starting from $N(\text{CH}_2\text{CH}_2\text{Cl})_3$ [5] and potassium pyrazolate with a procedure similar to that described for the synthesis of the methylated analogous ligand [1, 2]. The final dense oil was distilled at 196–198 °C at 2 mm Hg. *Anal.*: Calcd. for $\text{C}_{15}\text{H}_{21}\text{N}_7$: C, 60.18; H, 7.07; N, 32.75. Found: C, 60.4; H, 7.15; N, 33.1. The complexes were prepared using absolute ethanol, absolute ethanol-acetone mixture, acetone, or acetonitrile as solvents. In some cases diethyl ether was employed to promote crystallization of the products. A typical complex preparation has been carried out as follows. A warm solution of the ligand (10^{-3} mol in 20 cm^3 of the appropriate solvent) and a warm solution of the stoichiometric amount of NaBPh_4 (in the case of a tetraphenylborate complex) dissolved in 10 cm^3 of the same solvent, were added to a warm solution of the appropriate metal salt (10^{-3} mol in 30 cm^3 of the solvent). The solution of the reactants was concentrated by boiling and diethyl ether was added

TABLE I. Some Physical Data of the Complexes in the Solid State.

	$\mu_{\text{eff}} \mu_{\text{B}}^{\text{a}}$ (295 K) (90 K)	Absorp. Max., nm	Coord. Number
$[\text{VCl}(\text{TPyEA})]\text{BPh}_4$	3.54 2.93	525, 715	6
$[\text{V}(\text{NCS})_2(\text{TPyEA})]$	3.72	600	6
$[\text{CrBr}(\text{TPyEA})]\text{BPh}_4$	4.77 4.54	620, 985	6
$[\text{Fe}(\text{NCS})(\text{TPyEA})]\text{BPh}_4$	5.51	900, 1660	5
$[\text{CoBr}(\text{TPyEA})]\text{BPh}_4$	4.98 5.00	460 sh, 500, 525 sh, 580, 1025, 1250 sh	6
$[\text{CoBr}(\text{TPyEA})]\text{BPh}_4$	4.48 4.52	500 sh, 575, 880, 1750	5
$[\text{Co}(\text{NCS})_2(\text{TPyEA})]$	4.69	480, 525 sh, 625 sh, 1010	6
$[\text{Co}\{(\text{CH}_3)_2\text{CO}\}_2(\text{TPyEA})](\text{BPh}_4)_2$	4.52	475, 500 sh, 550, 1080, 1350 sh	6
$[\text{NiBr}(\text{TPyEA})]\text{BPh}_4$	3.24 3.38	375, 460 sh, 600, 1050	6
$[\text{Ni}(\text{NCS})_2(\text{TPyEA})]$	3.10	570, 940	6
$[\text{Ni}\{(\text{CH}_3)_2\text{CO}\}_2(\text{TPyEA})](\text{BPh}_4)_2$	3.21	370, 590, 985	6
$[\text{CuBr}(\text{TPyEA})]\text{BPh}_4$	1.81 1.85	650, 950	5

^a $1\mu_{\text{B}} = 9.27 \times 10^{-24}$ A m^2 . The values are per metal atom.

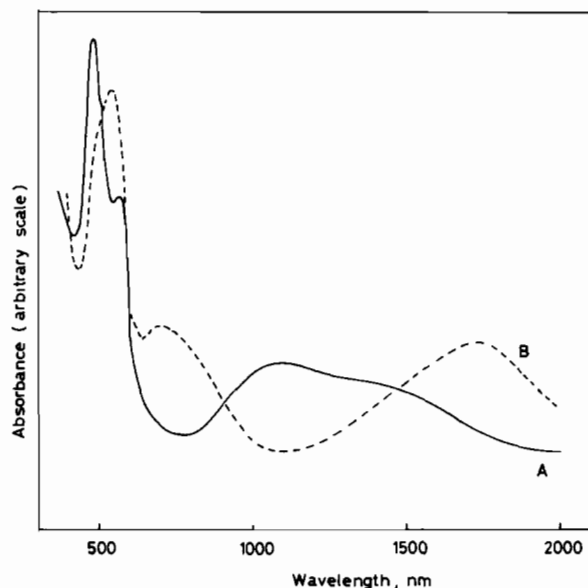


Fig. 1. Diffuse reflectance spectra of the $[\text{Co}(\text{acetone})_2(\text{TPyEA})](\text{BPh}_4)_2$ complex at 25 °C (curve A) and 89 °C (curve B).

until crystals of the complex separated. Recrystallization from acetone–diethyl ether, acetone–absolute ethanol, or acetonitrile–diethyl ether led to complexes with satisfactory elementary analyses. The complexes of vanadium(II), chromium(II), and iron(II) were prepared in anaerobic conditions.

Results

A number of complexes having the formulae $[\text{MX}(\text{TPyEA})]\text{BPh}_4$ ($\text{X} = \text{halide}$, pseudohalide, and other mononegative anions such as perchlorate and acetylacetonate) and $[\text{MX}_2(\text{TPyEA})]$ ($\text{X} = \text{halide}$, NCS^-) have been obtained with the various metal ions. With cobalt(II) and nickel(II), bis-solvento adducts $[\text{M}(\text{solvent})_2(\text{TPyEA})]\text{Y}_2$ ($\text{solvent} = \text{H}_2\text{O}$, CH_3CN , $(\text{CH}_3)_2\text{CO}$; $\text{Y} = \text{BPh}_4$ or Br) have also been obtained. The formulae of a few representative complexes are reported in Table I.

All of the complexes are high-spin and the assignment of the coordination geometry is quite straightforward for vanadium(II), iron(II), cobalt(II) and nickel(II) complexes on the basis of spectral evidence (Table I). The slight antiferromagnetic behaviour of the chromium(II) complexes, e.g. $[\text{CrBr}(\text{TPyEA})]\text{BPh}_4$ (Table I), and their insolubility in non-coordinating solvents lead us to assign them a six-coordinate geometry achieved through bridging anions in a dimeric or polymeric structure. The copper complexes appear to be mononuclear on the basis of

magnetic susceptibility and e.p.r. measurements, and consequently should be five-coordinate.

The nickel complexes $[\text{NiX}(\text{TPyEA})]\text{BPh}_4$ and $[\text{NiX}_2(\text{TPyEA})]$ are six-coordinate, irrespective of the nature of the co-ligand. The $[\text{CoX}(\text{TPyEA})]\text{BPh}_4$ derivatives on the other hand, are five-coordinate when $\text{X} = \text{I}$, NCS , NCO , ClO_4 and six-coordinate when $\text{X} = \text{F}$, Cl , Br , N_3 , acetylacetonate. Some of the six-coordinate cobalt(II) complexes are converted into five-coordinate isomers when heated in the solid state. The same transformation can occur on grinding the samples at room temperature.

Amongst the bis-solvento adducts obtained in the presence of the ligand TPyEA, the six-coordinate $[\text{M}\{(\text{CH}_3)_2\text{CO}\}_2(\text{TPyEA})](\text{BPh}_4)_2$ derivatives (CO stretch. freq.: 1690 sh, 1700 cm^{-1} , $\text{M} = \text{Co}$; 1686, 1697 cm^{-1} , $\text{M} = \text{Ni}$) are remarkable. Stable complexes containing acetone as co-ligands are quite rare [6]. Most acetone complexes are labile and therefore they cannot be isolated in the solid state. In these cases the acetone complexes with a variety of metals and ancillary ligands have been prepared *in situ* as useful precursors for the synthesis of metallo-organic complexes [7].

The red six-coordinate $[\text{Co}\{(\text{CH}_3)_2\text{CO}\}_2(\text{TPyEA})](\text{BPh}_4)_2$ derivative is stable at room temperature in the absence of moisture; when heated at $t < 90^\circ\text{C}$, it reversibly transforms into a magenta isomer which is five-coordinate on the basis of spectral evidence (Fig. 1). Moreover if the bis-acetone adduct is heated for a prolonged time at $t > 90^\circ\text{C}$ or is refluxed in a variety of solvents, a series of rearrangements of acetone molecules occurs which can be followed by i.r. spectroscopy. Studies are now under way to elucidate the nature of the reactions to which the bis-acetone complex gives rise and the compounds which are formed.

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