C – 310 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

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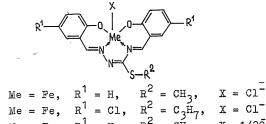
The dimensions of 2,2'bipyridine (bpy) and 1,10phenanthroline (phen) are such that a planar arrangement of two of these about a metal atom, with normal M-N distances, will result in an impossibly close approach of H-atoms of opposing ligands. The strain can be relieved by a tetrahedral distortion which twists the ligands out of the plane, or by keeping the metal and nitrogen atoms in a plane and tilting the ligands whilst retaining their planarity, or by a bow-shaped distortion of the ligands. Pt(phen) 2^+ (Hazell & Mukhopadhyay, Acta Cryst. (1980) <u>B36</u>, 1647) exhibits the twist deformation whereas (Pt(Dpy) 2^+ in its TCNO salts has the bow deformation (Dong, Endres et al., Acta Cryst. (1978) <u>B34</u>, 1823).

Pt(by)₂(NO₃)₂.H₂O is monoclinic, C2/c, with a = 19.257(3), b = 15.482(2), c = 7.071(1) Å, β = 101.55(1), and Z = 4. The structure was determined from 3393 reflexions [I>3σ(I)] and found to have the twist conformation. The structure is not isomorphous with the corresponding Pd compound (Chieh, J. Chem. Soc. Dalton Trans. (1972) 1643), but is isomorphous with the nitrate of Pt bpy phen²⁺ (Simonson (1984), private communication). The tetrahedral distortion is found to be smaller for the phenanthroline complexes than for those of 2-2'bipyridine.

Q9.4–32 THE COORDINATION ABILITY OF THIO-SEMICARBAZIDDIACETIC ACID. ITS METAL COMPLEXES. By I.F. Burshtein, T.I. Malinovsky, L.I. Petuchov, N.V. Gerbeleu, O.A. Bologa, Institute of Applied Physics, Institute of Chemistry of Moldavian Academy of Sciences, Kishinev, USSR.

Thiosemicarbazidacetic acid, $H_2NC(S)$ NHN (CH₂COOH)₂ = H₂L, is similar in structure to a well-known complexone – nitrilotriacetic acid. The residue L⁻² has six atoms capable of coordinating a metal. The following complexes of Co(II), Cu(II) and Cd(II) with H₂L have been studied by X-ray methods: CoL.H₂O (tricl., <u>I</u>, and rhomb., <u>II</u>); CoL.Thio (<u>III</u>); CuL (<u>IV</u>); CdL.4H₂O (<u>V</u>); CoLH₂.2H₂O (<u>VI</u>). Their crystallochemical features include: (1) The presence of monomeric (<u>I</u>, <u>III</u>, <u>VI</u>), dimeric (<u>V</u>) and polymeric (<u>IV</u>) structures. (2) The ability of the ligand to act as a O,O,N,S-tetradentate tripod ligand (<u>I</u> - <u>III</u>), a tetradentate and bridging ligand (<u>IV</u>, <u>V</u>), and a O,O,N,S-tetradentate tripod plus S-monodentate ligand iv<u>I</u> is the same as that of the free acid, but is different from the conformation of the molecule when it acts as a tripod ligand. The results permit us to suppose that H₂L differs from its nearest analog in the series of complexones (nitrilotriacetic acid) by forming more variable metal complexes, due to a specific set of donor atoms of H₂L. 09.4-33 STRUCTURE AND PROPERTIES OF Fe(III), Cu(II) AND Zn(II) COMPLEXES WITH TRI- AND TETRADENTATE LIGANDS DERIVED FROM S-ALKYLISO-THIOSEMICARBAZIDES. By <u>T.I.Malinowsky</u>, Yu.A. Simonov, M.A.Yampol'skaya, S.G.Shova, M.D.Revenko, V.G.Rusu, Institute of Applied Physics and Institute of Chemistry, Academy of Sciences, Moldavian SSR, Kishinev, USSR

The Fe(III) and Zn(II) compounds with tetradentate ligands derived from S-alkylisothiosemicarbazides have been obtained by the method of the template reactions.

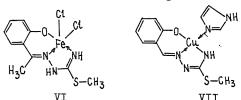


II	Me = Fe,	R	= Cl,	\mathbb{R}^2 =	C ₃ H ₇ ,	$X = C1^{-}$
III	Me = Fe,	\mathbf{R}^{1}	= H,	$R^2 =$	CH ₂ ,	$X = 1/20^{2}$
IV	Me = Fe, Me = Zn,	R ¹	= CH ₃ ,	$\mathbb{R}^2 =$	с ₄ н ₉ ,	$I = 1/20^{2}$
v	Me = Zn,	R^1	= H,	$\mathbb{R}^2 =$	CH ₃ ,	X = Py

Complexes I and II are molecular monomers with the tetragonal-pyramidal coordination of the metal. The average bond distances are the following: Fe-O = 1.884, Fe-N = 2.094 Å. The displacement of Fe ion from the N_2O_2 plane is 0.534 (I) and 0.549 Å (II). Complexes III and IV consist of dimeric mole-

Complexes III and IV consist of dimeric molecules in which iron ions are bonded by the Moxo-bridge. The Fe-ligand bond lengths are in good agreement with those observed in I and II. The geometric characteristics of the M-oxobridged system Fe-O-Fe are; Fe-O(M) = 1.769, 1.763 A, \angle Fe-O-Fe = 156.4, 157.89 for III and IV respectively.

1.763 Å, \angle Fe-O-Fe = 156.4, 157.89 for III and IV respectively. The Mössbauer spectra data and the temperature variation of the average susceptibility of the powdered samples show that the ground state of Fe(III) in I-IV is A. (S_i = 5/2). Zn(II) in the complex V has a pyramidal coordination similar to that of I and II. The crystal structure characteristics of I-V have been compared with those obtained early for Fe(III) and Cu(II) complexes (VI, VII) with related tridentate ligands.



The crystal data of the investigated complexes are shown in the table:

No	a	ъ	с	æ	ß	Y
I	7.933	16.943	12.181	90	90	91.76
II	9.331	9.445	12.807	80.48	68.93	89.79
III			14.275			120.49
IV	15.048	13.946	23.048	90	90	111.35
V	12.132	10.968	8.072	97.28	77.55	74.02
			12.072			69.42
VII	11.963	15.047	7.899	90	90	91.61