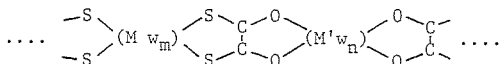


09.4-33 THE CRYSTAL STRUCTURE OF TETRABUTYLAMMONIUM TRISACETYLACETONATO-COBALTATE(II) AND -NICKELATE(II). By B. D. Santarsiero, A. Esmaili, V. Schomaker and E. C. Lingafelter, Department of Chemistry, University of Washington, Seattle, Washington 98195, U.S.A.

In the reported crystal structure of tetra-n-butylammonium trisacetylacetonato-cobaltate(II) (B. Granoff, Ph.D. dissertation, Princeton University, 1966) the cobalt-oxygen bond distances (mean 1.974(7)Å) appear to be unreasonably short. The structure has therefore been redetermined and, for comparison, the isomorphous nickel(II) compound has been investigated. The redetermination gives a mean cobalt-oxygen bond distance of 2.063(10)Å. In addition, several other significant differences have been noted between the original and the new structures, including a disordering of the cation. The space group is $P2_1/n$, the cell contains 4 molecules, and the cell dimensions are $a_0 = 9.933(3)$, $b_0 = 20.152(6)$, $c_0 = 18.403(8)$ Å, $\beta = 91.96(2)^\circ$ for the cobalt compound, and $a_0 = 9.967(2)$, $b_0 = 20.078(6)$, $c_0 = 18.317(6)$ Å, $\beta = 91.69(1)^\circ$ for the nickel compound.

09.4-34 CHAINES MOLECULAIRES HETEROPOLYMETALLIQUES. By A. Gleizes, Laboratoire de Chimie de Coordination du CNRS, Univ. Paul Sabatier, Toulouse, France, and M. Verdaguer, Laboratoire de Spectrochimie des Eléments de Transition, Univ. de Paris XI, Orsay, France.

Des composés de formule générale $MM'(dto)_2(w)_p$ ont été préparés: dto= dithiooxalate; M, M'= métal de transition; w= H₂O. Ce sont des prototypes d'une nouvelle classe de composés dont la structure à l'état solide est faite de chaînes hétéropolymétalliques parallèles:



Les couples métalliques mis en jeu et les valeurs de m, n et p-(m+n) sont les suivants:

Composé	M	m	M'	n	p-(m+n)
I	Ni(II)	0.08	Zn(II)	2	0
II	Ni(II)	0	Mn(II)	3	4,5
III	Pd(II)	0	Mn(II)	3	4,5
IV	Pt(II)	0	Mn(II)	3	4,5
V	Cu(II)	0	Mn(II)	3	4,5

Les structures cristallines ont été établies par diffraction $R\bar{X}$ sur monocristal pour les composés I (C2/m; $a=7,166(1)$ Å, $b=7,580(3)$ Å, $c=11,379(2)$ Å, $\beta=113,20(2)^\circ$; $R=0,036$) et II ($P2_1/c$; $a=11,575(2)$ Å, $b=20,654(6)$ Å, $c=7,323(1)$ Å, $\beta=103,73(1)^\circ$; $R=0,059$). D'après l'examen des clichés de diffraction sur poudre, les composés III, IV et V ont des structures analogues à celle de II.

Les propriétés magnétiques de ces composés seront présentées et discutées en relation avec les structures.

09.4-35 CRYSTAL STRUCTURE OF COBALT(III) COMPLEXES WITH MULTIDENTATE AMINE LIGANDS. By G. Bombieri, E. Forsellini and F. Benetollo, Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Padova (Italy) A. Del Pra, Istituto di Chimica Organica dell'Università, Padova (Italy).

The rate constants for the base hydrolysis of cobalt(III) complexes of the type $[Co(N_5)Cl]^{2+}$ where N₅ represents a combination of 5 primary, secondary or tertiary amine donor atoms coming from any combination of mono, bi, ter, quadri or pentadentate ligands is very sensitive to secondary features such as ligand configuration and ring size. The range of rate constants already reported in the literature covers at least 7 orders of magnitude [R.A.Henderson and M.L.Tobe, *Inorg. Chem.* **16**, 2576 (1977)]. In view of the large number of possible isomeric forms of some of these compounds it is essential to know, unambiguously, the detailed structures of the species examined and those reported in this communication are of considerable importance to the furtherance of the kinetic study. It has also been found that the presence of one or more pyridine donors within such a pentamine complex enhances the reactivity towards base hydrolysis even further. A knowledge of the isomeric form is therefore essential to any attempt to explain the role played by the pyridine.

We report here on the crystal and molecular structure of chloro(1,5,8,11,14-pentaazahexadecane)cobalt(III)perchlorate, $[Co([16]-N_5ane)Cl]^{2+}$, $2[ClO_4]^-$, bromo[1,9 bis(2-pyridyl) 2,5,8-triazanonane]cobalt(III)perchlorate, $[Co(picdien)Br]^{2+} \cdot 2[ClO_4]^-$, nitro[1,11 bis(2-pyridyl) 2,6,10-triazaundecane] cobalt(III) perchlorate, $[Co(picditn)NO_2]^{2+} \cdot 2[ClO_4]^-$.

$[Co([16]-N_5ane)Cl]^{2+}$, $2[ClO_4]^-$ is orthorhombic, space group $Fm\bar{2}1a$, $Z=4$, $a=14.317(7)$, $b=13.484(7)$ and $c=10.361(6)$ Å.

$[Co(picdien)Br]^{2+}$, $2[ClO_4]^-$ is monoclinic, space group $P2_1/a$, $Z=4$, $a=10.263(5)$, $b=27.845(9)$, $c=7.888(4)$ Å and $\beta=97.4(1)^\circ$.

$[Co(picditn)NO_2]^{2+}$, $2[ClO_4]^-$ is monoclinic, $Z=4$, $a=10.069(5)$, $b=28.514(9)$, $c=7.881(4)$ Å and $\beta=97.8(1)^\circ$.

The geometry of the $[Co([16]-N_5ane)Cl]^{2+}$ cation is a relatively undistorted octahedron. Within the pentadentate [16]-N₅ane ligand the six-membered ring assumes a chair conformation, while all five-membered rings are "gauche".

The coordination geometry of the $[Co(picdien)Br]^{2+}$ cation is near regular octahedral, with the pentadentate picdien ligand present in the α , β configuration [M.R.Snow, J. C. S. Dalton, 1627 (1972)]. Only two, i.e., one "angular" and the "flat" of the three secondary nitrogen atoms of the picdien ligand exhibit chirality and it is the same (SS and RR). Therefore the absolute configuration of the complex cation can be designated as Λ - α , β -S (and Λ - α , β -R). In both crystal structures the $[ClO_4]^-$ anion assumes a distorted tetrahedral configuration.

Bond distances and angles, the helicity of the conformation for the chelate rings as well as the coordination geometry of the $[Co(picditn)NO_2]^{2+}$ cation will be discussed.