

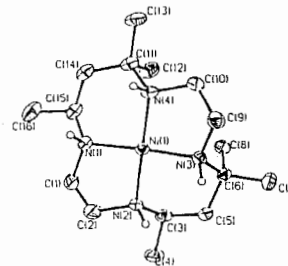
07-Crystallography of Organometallic and Coordination Compounds

PS-07.04.24 SIX CRYSTAL STRUCTURES OF Cu(II) AND Ni(II) PERCHLORATES WITH THE LIGANDS OF DIAMINO DIAZADECANES. By Kelun Shu* and Chung-Sun Chung, Department of Chemistry; Tahir. H. Tahirov and Tian-huey Lu, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, China.

The Cu(II) and Ni(II) complexes of aliphatic tetraamines have been extensively studied. However, these complexes containing alkyl groups on carbon or nitrogen have received very little attention. In order to study the steric effect of the N-alkyl or C-alkyl groups on the structures of Cu(II) and Ni(II) complexes, we have prepared and studied six crystal structures of the complexes. The six compounds are: (A), perchlorato[1,10-diamino-4,7-dimethyl-4,7-diazadecane]copper(II) perchlorate; (B), [1,10-diamino-4,7-dimethyl-4,7-diazadecane]nickel(II) diperchlorate; (C), diperchlorato[1,10-diamino-4-methyl-4,7-diazadecane]copper(II); (D), diperchlorato-[1,10-diamino-4,7-dimethyl-4,7-diazadecane]nickel(II); (E), [1-amino-4-methyl-10-isopropylamino-4,7-diazadecane]nickel(II) di-perchlorate and (F), perchlorato[1,10-diamino-6,6-dimethyl-4,7-diazadecane]copper(II) perchlorate, have been determined by X-ray diffraction. Their crystal data are: (A), orthorhombic, Pc_{2h} , $a=15.194(1)$, $b=15.135(1)$, $c=16.121(1)$ Å, $R=0.069$; (B), orthorhombic, $Pbca$, $a=14.585(1)$, $b=15.839(1)$, $c=16.218(1)$ Å, $R=0.075$; (C), monoclinic, $P2_1/n$, $a=8.790(1)$, $b=15.033(1)$, $c=13.463(1)$ Å, $\beta=102.22(2)^\circ$, $R=0.111$; (D), monoclinic, $P2_1/n$, $a=8.745(2)$, $b=13.687(3)$, $c=14.813(4)$ Å, $\gamma=100.07(2)^\circ$, $R=0.12$; (E), orthorhombic, $P2_12_12_1$, $a=8.491(4)$, $b=14.679(4)$, $c=16.827(3)$ Å, $R=0.055$; (F), monoclinic, $P2_1/n$, $a=13.297(1)$, $b=13.804(1)$, $c=10.136(1)$ Å, $\beta=91.05(1)^\circ$, $R=0.039$. Their coordination geometries for metal ions are: (A), five-coordinated; (B), four-coordinated; (C), six-coordinated; (D), six-coordinated; (E), four-coordinated; (F), five-coordinated. For the three Cu(II) complexes, (A), (C) and (F): comparing N(1)-Cu-N(3) bond angles, (C)>(F)>(A); comparing N(2)-Cu-N(4) bond angles, (F)>(A)>(C). The extent of distortion in (A) is larger than in (C) and (F). Owing to two methyl groups on the central two coordination nitrogens, the steric repulsion in (A) is stronger than in (C) and (F). For the three Ni(II) complexes, (B), (D) and (E); comparing N(1)-Cu-N(3) bond angles, (D)>(E)>(B); comparing N(2)-Cu-N(4) bond angles, (B)>(D)>(E). The extent of distortion in (E) is larger than in (B) and (D). Owing to one methyl on an internal nitrogen atom and the isopropyl on the terminal nitrogen atom, compound (E) has more steric repulsion than (B) and (D) resulting from high asymmetry. The hydrogen bonds among NH_2 groups and perchlorate O atoms help stabilize all the crystal structures. [Work was supported by National Science Council, Taiwan, China].

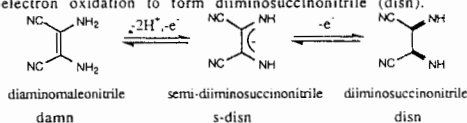
PS-07.04.25 CRYSTAL STRUCTURE OF HEXAMETHYL TETRAAZACYCLOTETRADECANE)NICKLE(II)•H₂O PERCHLORATE. By Tsong-Jen Lee, Arlohun Wang, Bor-Han Chen, Yi-Zhong Yuan and Chung-Sun Chung, National Tsing Hua University, Hsinchu, 30043 Taiwan.

β -meso-(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclopentadecane)Nickel(II)•H₂O Perchlorate, $NiN_4C_{16}H_{36}(ClO_4)_2 \cdot (H_2O)$, $Mr=560.12$, monoclinic, $P2_1/a$, $a=17.388(2)$, $b=9.172(4)$, $c=17.494(2)$ Å, $\beta=116.717(7)^\circ$, $U=2492.2$ Å³, $Z=4$, $D_x=1.49$ g/cm³, $\lambda(Mo K_\alpha)=0.71073$ Å, $\mu=13.56$ mm⁻¹, $F(000)=1184$, $T=300(5)$ K, $R=0.062$, $R_w=0.062$ for 2660 observed reflections [$I>3\sigma(I)$]. The Ni(II) ion is four-coordinated with nitrogen atoms of the macrocyclic ligand, they are coplanar within 0.04(1) Å. As shown in the ORTEP plot, the four H atoms on the amine groups are on the same side of the macrocyclic plane. The configuration of the four chiral nitrogen centers and two chiral carbon centers are (1RS, 4SR, 8RS, 11SR) and (5SR, 14RS) respectively. The two five membered chelate rings are in a slightly distorted gauche form and the two six-membered chelate rings in a stable chairform.



PS-07.04.26 Trigonal Prismatic Coordination Chemistry
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Many of interesting and important features of transition metal complexes containing semi-benzoquinonediimine ligands are related to the similarity in energy between the benzoquinonediimine π^* -orbitals and the metal d-levels. Reacting with metal ion under basic condition, diaminomaleonitrile (damn) deprotonates easily in the presence of oxygen to form semi-diaminosuccinonitrile (s-disn) or two-electron oxidation to form diaminosuccinonitrile (disn).



In this paper, we present the synthesis and reaction of rhenium & molybdenum complexes of the s-disn ligand and the characterization by X-ray crystallography of the unusual compound $[Re^{IV}(s-disn)_3]_2[Re^{III}(s-disn)_3]_2[Re^{VII}O_4]_2[Re^{VII}O_7](OEt)_3$. The reaction of $HReO_4$ with diaminomaleonitrile (damn) (2:3) in CH_3CN leads to the formation of a blue solution. Blue crystals, $[Re^{IV}(s-disn)_3]^+[Re^{VII}O_4]^-$, were obtained after addition of ether to the solution. The blue species $[Re^{IV}(s-disn)_3]^+$ is gradually reduced by longer standing (e.g. a couple days) to $[Re^{III}(s-disn)_3]^0$ which is crystallized out as black purple crystals. The mixed dark blue metal complexes $[Re^{IV}(s-disn)_3]_2[Re^{III}(s-disn)_3]_2[Re^{VII}O_4]_2[Re^{VII}O_7](OEt)_3$ was crystallized out by addition of ether to the blue solution after few hours. The bonding and structure in the diaminosuccinonitrile ligand is of particular interest. The imine C-N bond (av. 1.326 Å) consists with their identification as delocalized bonds. The structure of both Re complexes, $[Re^{IV}(s-disn)_3]^+$ and $[Re^{III}(s-disn)_3]^0$ exhibit a trigonal prismatic geometry.

The reaction of $Mo(CO)_6$ with diaminosuccinonitrile (disn) (1:3) in CH_3CN leads to the formation of a blue crystal, $[Mo^{III}(s-disn)_3]^0$. It is isolectronic with $[Re^{IV}(s-disn)_3]^+$ and isostructural with $[Re^{III}(s-disn)_3]^0$. It is believed that $[Mo^{III}(s-disn)_3]^0$ also exhibit a trigonal prismatic coordination.