



References

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CRYSTAL STRUCTURES OF COPPER(II) TETRACYANIDOPLATINATES

M. Vávra, I. Potočňák

Department of Inorganic Chemistry, Institute of Chemistry, P.J. Šafárik University, Moyzesova 11, SK-04154 Košice, Slovakia

Introduction

The cyanide moiety C N can act as a terminal or bridging ligand in cyanidometallate complexes. In most compounds with bridging cyanide, polymeric one- (1D), two- (2D) or three-dimensional (3D) networks are observed in the solid state, moreover a lot of poly-nuclear zero-dimensional (0D) compounds are observed, too [1]. All compounds, which dimensionality is not 3D, are considered as low-dimensional.

Results and discussion

We have prepared and structurally characterized a series of low-dimensional complexes with $[\text{CuL}_n][\text{Pt}(\text{CN})_4]$ general composition (L are neutral polydentate N -donor ligands and n is 1 or 2) within our study of the crystal structures and properties of copper(II) tetracyanidoplatinates. These compounds can be divided, according to the covalent bonds, to 0D, 1D and 2D. 0D complexes differ from each other in the number of metal atoms in individual complex cations. The most simple one, $[\text{Cu}(\text{tacn})_2][\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (**1**) (tacn = tridentate 1,4,7-triazacyclononane), contains mono-nuclear cation (Fig. 1a). We have also prepared two complexes with tri-nuclear cations of $\{[\text{CuL}]_2[\text{Pt}(\text{CN})_4]\}^{2+}$ composition (L are either two bidentate 1,2-animopropane (pn) (**2**) or one tetradentate triethylenetetramine ligands (**3**)) (Fig. 1b) and one complex, $\{[\text{Cu}(\text{tn})_2]_3[\text{Pt}(\text{CN})_4]_2\}[\text{Pt}(\text{CN})_4]$ (**4**) (tn = 1,3-diaminopropane), with the complicated five-nuclear cation (Fig. 1c). All mentioned poly-nuclear complex cations contain $[\text{Pt}(\text{CN})_4]^{2-}$ particles with two terminal and two bridging cyanido groups.

The highest variability of the structures exhibit 1D compounds. All our prepared 1D complexes can be described as simple chains which consist of $[\text{CuL}_n]^{2+}$ moieties bridged by two cyanido groups of $[\text{Pt}(\text{CN})_4]^{2-}$ units. The number and a mutual position of bridging cyanido groups in the cationic and anionic particles are specified by a pair of digits and by symbols „T” (*trans*) or „C” (*cis*). Thus, as an example, the 2,2-TC symbol means a chain with two bridging cyanido groups *trans*-coordinated in the $[\text{CuL}_n]^{2+}$ species and two bridging cyanido groups *cis*-coordinated

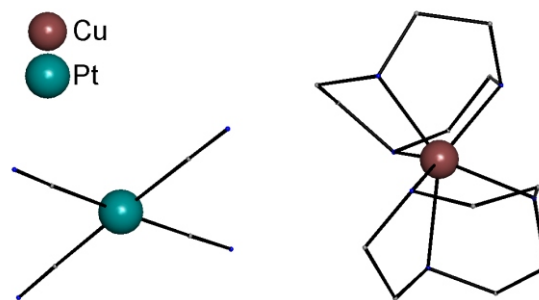


Figure 1a. Structure of 1 with mono-nuclear complex cation.

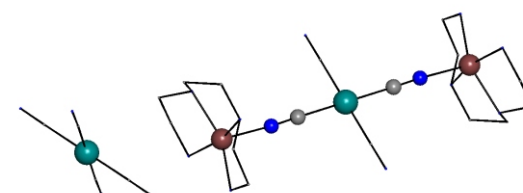


Figure 1b. Structure of 3 with tri-nuclear complex cation.

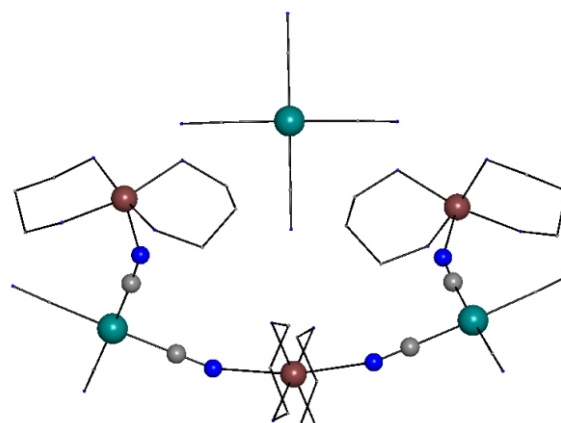
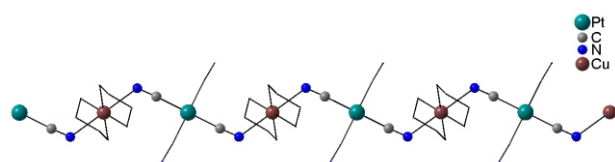
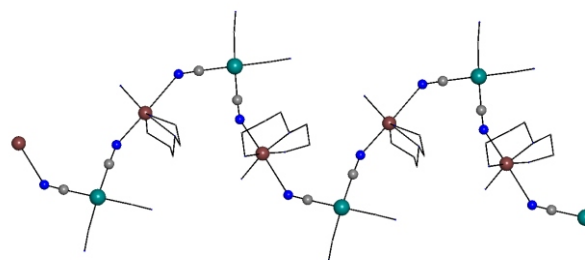
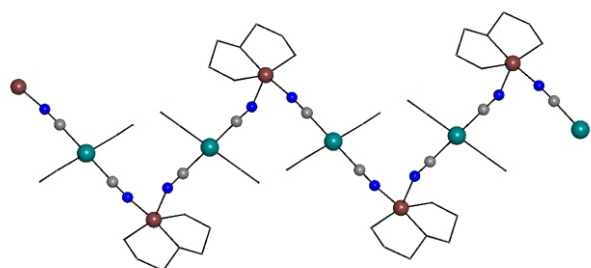
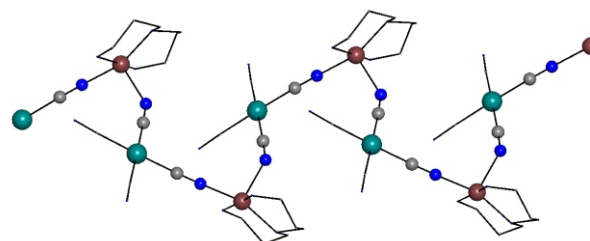


Figure 1c. Structure of 4 with penta-nuclear complex cation.


 Figure 2a. 2,2-*TT* chain in 5.

 Figure 2b. 2,2-*TC* chain in 6.

 Figure 2c. 2,2-*CT* chain in 8.

 Figure 2d. 2,2-*CC* chain in 9.

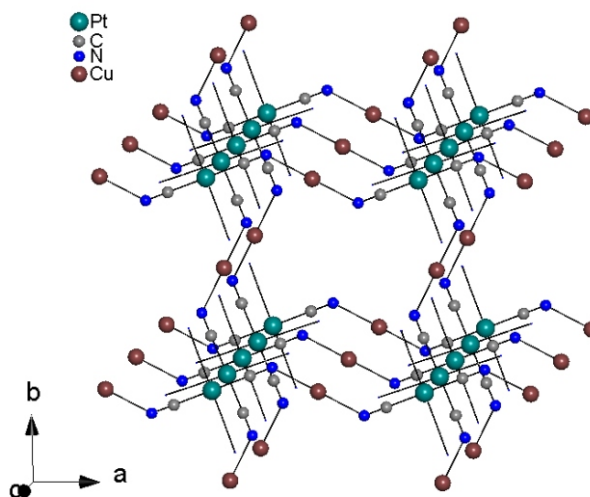
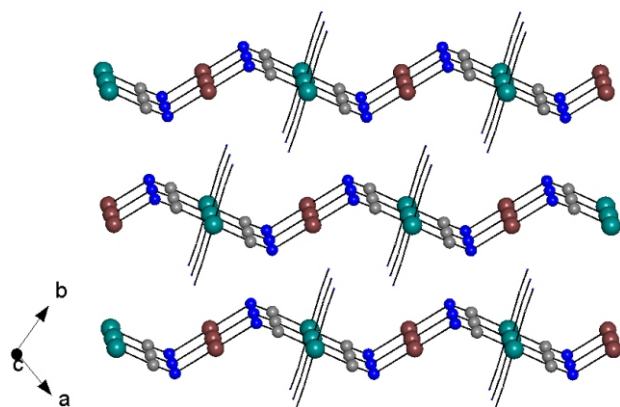
in the $[\text{Pt}(\text{CN})_4]^{2-}$ part [for detailed nomenclature see 2]. We have prepared compounds with all four possible types of chains (Figs. 2a – 2d). Prepared chains are not linear but zig-zag not only due to the *cis*-coordination, but also due to the nonlinearity of the Cu–N–C bond angles.

The most probable and also most observed type of the chain is 2,2-*TT* type, which was observed in six prepared compounds; as an example $[\text{Cu}(\text{en})_2][\text{Pt}(\text{CN})_4]$ (**5**) complex (*en* = 1,2-diaminoethane) is shown in Fig. 2a. Equatorial plane in these complexes is occupied by four nitrogen atoms from *L*, while axial positions are free for bridging cyanido groups of $[\text{Pt}(\text{CN})_4]^{2-}$ particles. As blocking *N*-donor ligands *L*, two molecules of bidentate *en* and its three different methyl derivatives as well as one tetradentate ligand 1,4,8,11-tetraazacyclotetradecane were used. An interesting situation occurs in the system with mono-methyl derivative of *en* (*men*) as two different compounds with the same $[\text{Cu}(\text{men})_2][\text{Pt}(\text{CN})_4]$ composition were isolated (violet and blue crystals). The violet modification crystallizes in triclinic *P*-1 space group, while the blue modification in tetragonal *P*₄/*m* group. The most striking difference in

these two structures is a different packing of the chains. Whereas all chains in the triclinic modification run along the [1 1 1] direction being thus mutually parallel (Fig. 3, left), the chains in the tetragonal modification are extended along both the *a* and *b* axes. Thus two sets of parallel chains which are perpendicularly crossed exist (Fig. 3, right).

Next type of a simple 2,2 chain is unusual 2,2-*TC*, observed in the $[\text{Cu}(\text{NH}_3)(\text{aepn})][\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ (**6**) complex (*aepn* = 3-(2-aminoethylamine)-propylamine) (Fig. 2b). Like in 2,2-*TT*, equatorial plane of the copper atom is occupied by *N*-donor ligands and bridging cyanido groups are *trans*-coordinated in the axial positions. However, the bridging cyanido groups occupy *cis*-positions on the platinum atom.

If *N*-donor ligands occupy both the equatorial and axial positions around the copper atom, the *cis*-coordination of two bridging cyanido groups is expected. Within our re-


 Figure 3. Different packing of $[\text{Cu}(\text{men})_2][\text{Pt}(\text{CN})_4]$ chains; left – triclinic system, right – tetragonal system.

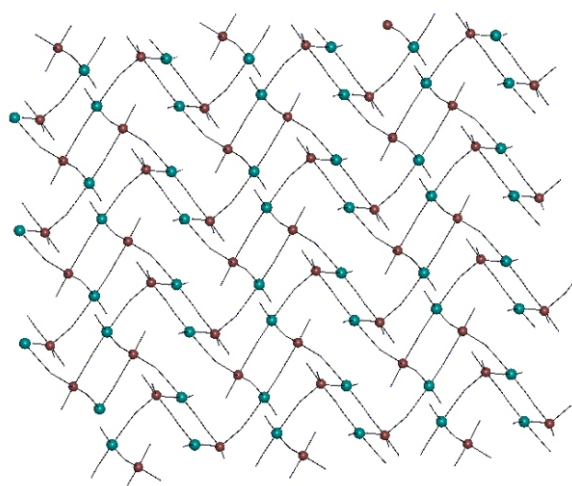


Figure 4a. 2D network with three bridging cyanido groups in **12**.

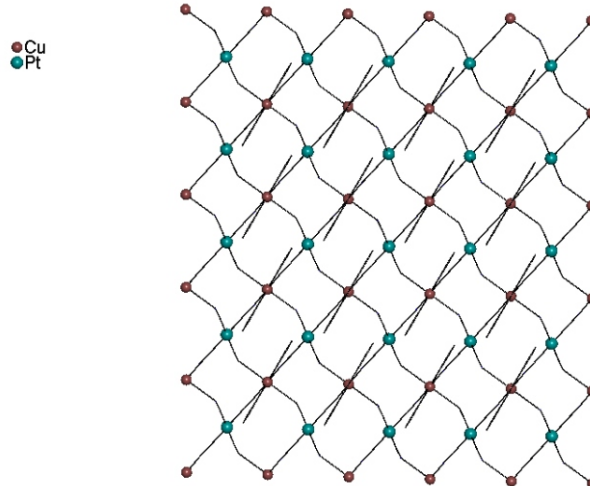


Figure 4b. 2D network with all four bridging cyanido groups in **13**.

search, two complexes (**7** - $[\text{Cu}(\text{bpy})_2][\text{Pt}(\text{CN})_4]$ (*bpy* = 2,2'-bipyridine) and **8** - $[\text{Cu}(\text{dien})][\text{Pt}(\text{CN})_4]$ (*dien* = bis(2-aminoethyl)amine)) of 2,2-*CT* type (Fig. 2c) and two complexes (**9** - $[\text{Cu}(\text{aepn})][\text{Pt}(\text{CN})_4]$ and **10** - $[\text{Cu}(\text{bapa})][\text{Pt}(\text{CN})_4]$, where *bapa* is bis(3-aminopropyl)-amine) of 2,2-*CC* type (Fig. 2d) have been characterized. It is important to note, that compounds with 2,2-*CC* chain containing $[\text{Pt}(\text{CN})_4]^{2-}$ particles have not been observed in the literature up to now.

If three or more bridging cyanido groups are bonded to the central metal atoms, 2D structures are formed and we have observed two types of different networks of the same $[\text{CuL}][\text{Pt}(\text{CN})_4]$ composition. If only three cyanido groups are bridging, first type of the network is formed (Fig. 4a). Coordination number of the copper atom is five in that case and the two remaining positions occupies bidentate ligand *L*, either *pn* (**11**) or bulky tetramethyl *N*-derivative of *en* (**12**). The second type is more regular because all four cyanido groups are bridging and a square network occurs (Fig. 4b). Thus, coordination number of the copper atom is six and last two positions occupies a molecule of aromatic 1,10-phenanthroline, as ligand *L* (**13**).

Conclusion

Low-dimensional $[\text{CuL}_n][\text{Pt}(\text{CN})_4]$ complexes are according to the covalent bonds divided into the 0D, 1D and 2D. Zero-dimensional complexes are formed by several types of poly-nuclear ionic complexes. Each 1D complex can be classified as 2,2 chain with two bridging cyanido groups on both copper and platinum atoms. All four possible types of the chains were observed in our research. 2D complexes are formed by two different types of networks with three or four bridging cyanido groups.

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