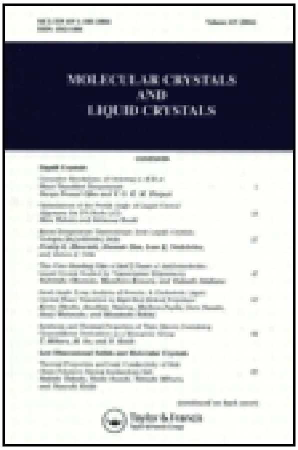

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$H_2Pt(CN)_4$ and Derivative H^+ Solvates and Defect Structures

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$H_2Pt(CN)_4$ AND DERIVATIVE H^+ SOLVATES AND DEFECT STRUCTURES

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Abstract Tetracyanoplatinates with protonated alcohol, amine, and glycine molecules as cations were prepared. The structures were studied with respect to formation of isostructural, partially oxidized phases. Unsolvated $H_2Pt(CN)_4$ was prepared and characterized.

INTRODUCTION

Charges and sizes of cations are of special importance for columnar structures of tetracyanoplatinates (tcp), since columnar stacking implies restrictions for the arrangements of negative charges (mainly on cyanide N atoms); that is all the more true for partially oxidized (po) phases with Pt-Pt distances less than 3.0 Å and is the main reason why po phases are not simply cation defect or anion doped versions of unoxidized phases. Their much smaller columnar repeat distance requires a different structure in order to provide the cation with a proper coordination sphere.

The smallest cation H^+, however, behaves otherwise, because it can be solvated by molecules of different shapes and sizes, and its coordination number is two, normally. If the solvated cation contains more than one H, positive charge could be delocalized. Related isostructural po structures might be obtained by producing proton defects. Only anion doped po phases of tcp have been described so far: ammonium[1] and guanidinium[2] tetracyanoplatinate.

ROH SOLVATES AND $H_2Pt(CN)_4$

Evaporation of aqueous solutions of $H_2Pt(CN)_4$, easily made by ion exchange of salt solutions leads to unseparable mixtures of differently colored phases. By dissolving these mixtures in alcohols, a series of crystallizable solvates were prepared. With CH_3OH, no solvate could be isolated; solvate phases with other alcohols are described in Table 1. A single crystal structure determination of $(C_2H_5OH_2)_2$tcp[3] showed H bridging of cations between tcp chains. n-$(C_3H_7OH_2)_2$tcp is isostructural with greater c value due to the large alkyl group. Columnar solvate structures were also obtained with bifunctional molecules like HOC_2H_4OH and $H_2NC_2H_4OH$. All observed structures, (2) to (5) in Table 1, appear to be unfavorable for the formation of related isostructural po phases.

Desolvating $(ROH_2)_2$tcp yields unsolvated H_2tcp as a yellow polycrystalline compound, (1) in Table 1, which reacts with moist air to an unrelated po phase $(H_3O)_{1.8}$tcp.[3]

GLYCINE SOLVATES

The protonated form of aminoacetic acid (glycine, gly) exists in strongly acidic solutions. This cation $glyH^+$ is component of some tcp salts. Their composition and single crystal data are given in Table 1, (6)(7). Under less acid conditions and in the presence of NH_4^+, salts with glyH and NH_4 cations are formed, (9)(10). Almost neutral reaction mixtures lead to (gly)$(NH_4)_2$tcp, (11).

Crystal structures have been determined for (6) and (7). The latter is a columnar structure, which can be oxidized to a related isostructural po phase (8), which is being studied. The Pt distance shrinks from 3.17 Å in (7) to 2.95 in (8), while a and b constants slightly increase.

ETHYLENEDIAMMONIUM TETRACYANOPLATINATE

With ethylenediamine (en) and aqueous H_2tcp, yellow (enH_2)tcp(H_2O) was prepared. A crystal structure determination (12)[4] found RNH_3 protons alone taking part in H bridges between chains. Optical

TABLE 1 Crystal data of $H_2Pt(CN)_4$ and solvates studied

	formula	a alpha	b beta	c /Å gamma	Pt distance; remarks
(1)	H_2tcp	8.75	8.75	7.58	not columnar; yellow
	tetragonal				
(2)	$(C_2H_5OH_2)_2$tcp	14.28	14.28	6.49	3.25; red
	tetragonal				
(3)	$(C_3H_7OH_2)_2$tcp	14.21	14.21	7.30	3.65; colorless
	tetragonal				
(4)	$(H_2OC_2H_4OH_2)$tcp	14.44	14.44	13.36	3.34; orange
	tetragonal				
(5)	$(H_3NC_2H_4OH_2)$tcp	9.67	9.73	14.08	3.52; colorless
	triclinic	93.1	94.2	90.8	
(6)	$(glyH)_2$tcp	8.15	16.43	5.04	not columnar; colorl.
	monoclinic	90	90	97.67	
(7)	(glyH)(H_3O)tcp	13.47	13.47	19.04	3.17; dark red
	tetragonal				
(8)	$(glyH)_x(H_3O)_y$tcp	13.76	13.76	5.90	2.95; dark brown
	tetragonal				
(9)	(glyH)(NH_4)tcp	13.63	13.63	10.65	3.55; greenish
	tetragonal				
(10)	$(glyH)_3(NH_4)(tcp)_2$	9.60	22.93	20.40	3.24; orange
	monoclinic	90	109.2	90	
(11)	$(NH_4)_2$(gly)tcp	12.84	12.84	10.21	3.40; yellow
	monoclinic	90	90.8	90	
(12)	(enH_2)tcp$(H_2O)_{0.5}$	13.08	16.24	9.51	3.27; yellow
	orthorhombic				

tcp = $Pt(CN)_4$ gly = glycine en = ethylenediamine properties have already been reported.[5]

Anodic oxidation leads to a po phase with similar sublattice dimensions except the chain direction a, which decreases giving Pt-Pt 2.95 Å. Closer examination (still under way) revealed a very complicated 3D superstructure and no simple proton defect structure since the composition is $(enH_2)_{0.84}(H_3O)_{0.14}tcp(H_2O)_{0.5}$.

REFERENCES

1. P.L. Johnson, A. J. Schultz, A. E. Underhill, D. M. Watkins, D. J. Wood, and J. M. Williams, Inorg. Chem., 17, 839 (1978).
2. G. D. Stucky, C. Putnik, J. Kelber, M. J. Schaffman, M. B. Salamon, G. Pasquali, A. J. Schultz, J. M. Williams, T. F. Cornish, D. M. Washecheck, and P. L. Johnson, Ann. N. Y. Acad. Sci., 313, 525 (1978).
3. A. Keim, Thesis, Uni Karlsruhe (1984).
4. H. P. Pfleger, Thesis, Uni Karlsruhe (1981).
5. R. Dillinger, G. Gliemann, H. P. Pfleger, and K. Krogmann, Inorg. Chem., 22, 1366 (1983).