

to varying population of vibrational levels as a function of temperature^{15a} or rotation and oscillation in the matrix.^{15b}

(15) (a) S. I. Chan, private communication; (b) E. Wasserman, private communication.

(16) John and Beverly Stauffer Foundation Fellow, 1975–1976.

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On the Alleged Existence of Partially Oxidized Mg[Pt(CN)₄]Cl_{0.28}·7H₂O and the Attempted Preparation of the Analogous Be²⁺ and Ba²⁺ Derivatives. A Caveat¹

Sir:

Partially oxidized tetracyanoplatinate (POTCP) conducting salts of *monovalent* cations are well known,^{2a,b} and we have recently reported the unusual molecular structures of *anion* deficient K₂[Pt(CN)₄]Br_{0.3}·3H₂O,^{2c} KCP(Br), and *cation* deficient K_{1.75}[Pt(CN)₄]·1.5H₂O,^{2d} K(def)TCP. These one- and quasi-one-dimensional salts form unusual Pt–Pt “chains” having metal–metal separations not greatly in excess of that observed in platinum metal itself. In an effort to understand the effect of cation size on the structure, the conductive properties, and the Pt–Pt bond lengths, we have undertaken

the synthesis and characterization of POTCP salts containing a *divalent* cation.

There exists in the literature only one recent report of a POTCP salt of a *divalent* cation, viz., *blue* Mg[Pt(CN)₄]Cl_{0.28}·7H₂O,^{3,4} hereafter referred to as **1**. The preparation of **1** was reportedly accomplished³ by cocrystallizing red Mg[Pt(CN)₄]·7H₂O, hereafter known as **2**, and Mg[Pt(CN)₄]Cl₂·xH₂O. Initially we attempted the room temperature synthesis of the corresponding POTCP complexes of Be²⁺ and Ba²⁺ but were unable to form partially oxidized complexes. Therefore, the Krogmann and Ringwald³ synthesis of **1** was repeated, and we did indeed obtain the “blue magnesium tetracyanoplatinate” they reported. However, this material transformed to crystalline **2** depending simply on the H₂O vapor pressure above the sample. Thus it appears that the material thought to be the only POTCP of a *divalent* cation is simply a different hydrate of Mg[Pt(CN)₄]·7H₂O. We have further verified the composition of the compounds and the lack of halogen by chemical analysis,⁵ x-ray fluorescence studies, and powder x-ray diffraction (*vide infra*). The implications of these results with respect to the formation of one-dimensional POTCP salts of Be²⁺, Mg²⁺, and Ba²⁺ are discussed herein.

Partial oxidation of dark-red Be[Pt(CN)₄]·2H₂O, **3**, by cocrystallization of Be[Pt(CN)₄]Br₂·xH₂O and **3** at room temperature, yielded only a mixture of starting materials. Similarly, attempted partial oxidation of yellow-green-Ba[Pt(CN)₄]·4H₂O, **4**, by cocrystallization of Ba[Pt(CN)₄]Br₂·5H₂O and **4** at room temperature, and alternatively

Table I. X-Ray Diffraction Powder Patterns of Magnesium Tetracyanoplatinates^a

Mg[Pt(CN) ₄]Cl _{0.28} ·7H ₂ O ³ (blue)	Mg[Pt(CN) ₄]·xH ₂ O ^b (blue)	Mg[Pt(CN) ₄]·7H ₂ O ³ (red)	Mg[Pt(CN) ₄]·xH ₂ O ^c (red-green) ¹⁶	Mg[Pt(CN) ₄]·xH ₂ O ^d (dark-purple)
4.2 (vs)	4.2 (vs)	4.0 (vs)	4.3 (vs)	4.2 (vs)
6.0 (vs)	6.0 (vs)	6.0 (vs)	6.1 (vs)	6.0 (vs)
8.6 (vs)	8.6 (vs)	8.6 (vs)	8.6 (vs)	8.6 (vs)
9.6 (vs)	9.6 (vs)	9.3 (w)	9.3 (w)	
10.0 (vw)		9.6 (vs)	9.7 (vs)	9.6 (vs)
		11.1 (w)	11.2 (w)	
		11.6 (vw)	11.8 (vw)	
		12.0 (vw)		
12.1 (m)	12.2 (m)	12.3 (s)	12.3 (s)	12.2 (s)
		12.6 (vw)		
12.9 (w)	12.9 (w)	12.9 (s)	13.0 (s)	13.0 (m)
		13.1 (vw)		
13.6 (m)	13.6 (m)	13.7 (s)	13.8 (s)	13.7 (m)
14.2 (vw)	14.4 (vw)	14.2 (w)	14.2 (w)	14.1 (vw)
		14.5 (vs)	14.6 (s)	
14.6 (vw)	14.7 (vw)	14.8 (vw)	15.2 (w)	14.7 (vw)
15.0 (vw)				15.1 (vw)
15.3 (s)	15.2 (m)			
15.5 (m)	15.6 (w)			15.6 (s)
		15.8 (vs)	15.8 (vs)	
16.5 (s)	16.4 (m)			16.8 (m)
17.3 (w)	17.3 (w)			17.4 (w)
17.6 (m)	17.6 (w)			
17.9 (m)	17.9 (w)			18.0 (m)
18.3 (w)	18.4 (w)			18.5 (w)
18.7 (m)	18.7 (w)			
				19.0 (w)
19.4 (w)	19.5 (w)			
19.7 (m)	19.7 (w)			
21.6 (s)	21.6 (m)			20.0 (m)
21.8 (w)	21.9 (m)			21.9 (s)

^a Diffraction lines are reported in degrees θ and vs = very strong; s = strong; m = medium; w = weak; vw = very weak. Argonne patterns taken with Cu K α radiation, λ 1.5418 Å. ^b Prepared by cocrystallizing Mg[Pt(CN)₄]·7H₂O and Mg[Pt(CN)₄]Cl₂·xH₂O (this work). ^c Red-green¹⁶ crystals formed after the blue^b magnesium tetracyanoplatinate was removed from the solution in which it was prepared and stored at 72% relative humidity (this work). This pattern was identical with that of Mg[Pt(CN)₄]·7H₂O prepared in this study. ^d Prepared by the addition of H₂O₂ to a solution of Mg[Pt(CN)₄]·7H₂O.

Table II. Rates of Transformation of Blue Magnesium Tetracyanoplatinate to Red-Green¹⁶ Magnesium Tetracyanoplatinate

Saturated salt solution	Relative humidity	Transformation time
NH ₄ Cl and KNO ₃	72% at 23° ^a	~1 h
(NH ₄) ₂ SO ₄	80% at 25° ¹⁰	~1 day
BaCl ₂ ·2H ₂ O	90% at 25° ¹⁰	~4 days

^a G. Edgar and W. O. Swan, *J. Am. Chem. Soc.*, **44**, 570 (1922).

by the addition of H₂O₂ to a solution of **4** in the presence of HBr, yielded only green crystals. These green crystals were shown by chemical analysis⁶ to be unoxidized Ba[Pt(CN)₄]·4H₂O, in agreement with the previous report by Levy.⁷

The "blue magnesium tetracyanoplatinate" described by Krogmann and Ringwald³ was easily prepared by their method and an x-ray diffraction powder pattern of this material was identical with that which they reported (see Table I). However, chemical analysis for chlorine revealed that only trace amounts (<0.1%) were present.⁸ In addition, no Cl⁻ was detected by x-ray fluorescence spectroscopy.⁹ Subsequently it was discovered that when the "blue Mg[Pt(CN)₄]Cl_{0.28}·7H₂O" was removed from the solution in which it was prepared, and stored over a saturated barium chloride solution (relative humidity¹⁰ of 90% at 25 °C), the blue crystals transformed slowly to red-green¹⁶ crystals. An x-ray diffraction powder pattern of this red-green material was identical with the pattern of the nonhalogenated red Mg[Pt(CN)₄]·7H₂O prepared by the authors, and to the pattern of **2** reported by Krogmann and Ringwald³ (see Table I).

Handling of the blue magnesium tetracyanoplatinate is difficult because the hydration state apparently changes easily and rapidly; e.g., addition of water to the blue material in its preparative solution results in the formation of a white precipitate. This handling problem greatly complicates the chemical analysis, but the material does appear to be nearly a 7–8 hydrate. The relative rate at which the blue material transforms to the red-green variety, at room temperature under differing relative humidities, is shown in Table II. Our attempts to grow large crystals of the blue magnesium tetracyanoplatinate have been unsuccessful, in agreement with a report by Krogmann.^{2b}

Other hydration states which we have observed for the transformed blue material include a blue-green phase, a violet phase, and a bright-red phase. These complex hydrate phases of Mg[Pt(CN)₄]·7H₂O have previously been reported.¹¹ The wide range of color changes exhibited by **2** is related to the interplanar Pt(CN)₄²⁻ distances as was first pointed out by Yamada,¹² and the great ease with which many of the platinumocyanides "dehydrate (below 100 °C) and thereby reorganize themselves in order to form a new structure . . . as shown by spectacular color changes" has been reported by Moreau-Colin.¹³

An additional report which corroborates our results with Mg²⁺ platinumocyanide complexes is based on an 1856 report by Weselsky¹⁴ who mentioned a "blackish violet" partially oxidized magnesium pentacyanoplatinate, Mg[Pt(CN)₅]·7H₂O, prepared by the partial oxidation of Mg[Pt(CN)₄]·7H₂O by HNO₃. In an alternate attempt to prepare this Mg²⁺ platinumocyanide complex, we have prepared a dark purple solid by the addition of H₂O₂ to a solution of **2**. We were surprised to find that an x-ray diffraction powder pattern of this material was nearly identical with the x-ray powder pattern of blue compound **1** reported by Krogmann and Ringwald³ (see Table I). When this dark purple material was removed from the solution in which it was prepared, it transformed to green crystals. Thus it appears that this dark purple magnesium pla-

tinocyanide is also a different hydrate of Mg[Pt(CN)₄]·7H₂O.

It therefore appears that POTCP complexes of *divalent* cations have yet to be prepared. In the specific case of the magnesium tetracyanoplatinates, the bulky, hydrated magnesium cations may sufficiently hinder the close approach of planar Pt(CN)₄²⁻ groups, and concomitant overlap of the Pt(5d_z²) orbitals, which appears to be essential for the formation of short Pt–Pt chains observed in the *monovalent* alkali metal salts.^{2b} The observed inability to prepare POTCP salts of *divalent* cations may provide invaluable insight into the relative importance of cation charge and cation solvation effects on the formation of these salts. Such effects should be considered in future synthetic efforts directed toward the formation of highly conducting one-dimensional tetracyanoplatinates.

References and Notes

- (1) Work performed under the auspices of the U.S. Energy Research and Development Administration.
- (2) See, for example, (a) L. A. Levy, *J. Chem. Soc.*, **101**, 1081 (1912); T. W. Thomas and A. W. Underhill, *Chem. Soc. Rev.*, **1** (1), 99 (1972); (b) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969); (c) J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Peterson, *Phys. Rev. Lett.*, **33** (18), 1079 (1974); (d) K. D. Keefer, D. M. Washecheck, N. P. Enright, and J. M. Williams, *J. Am. Chem. Soc.*, **98**, 233 (1976).
- (3) K. Krogmann and G. Ringwald, *Z. Naturforsch. B*, **23**, 1112 (1968).
- (4) D. Kuse, *Solid State Commun.*, **13**, 887 (1973).
- (5) All chemical analyses were performed by Midwest Microlab, Indianapolis, Ind.
- (6) Anal. Calcd for C₄H₈N₄O₂BaPt: C, 9.45; H, 1.59; N, 11.02. Found: C, 9.60; H, 1.59; N, 11.17; Br, 0.0.
- (7) L. A. Levy, *J. Chem. Soc.*, **93**, 1454 (1908).
- (8) Anal. Calcd for C₄H₁₄N₄O₇MgPt: C, 10.45; H, 3.07; N, 12.20; O, 24.37; Cl, 2.16. Calcd. for C₄H₁₄N₄O₇MgPt: C, 10.69; H, 3.14; N, 12.46; O, 24.91. Found: C, 10.82; H, 2.49; N, 12.90; O, 24.77; Cl, 0.0.
- (9) X-Ray fluorescence spectroscopy performed by Dr. A. Reis, Jr., and R. L. Maffly at the Chemistry Division, Argonne National Laboratory.
- (10) J. F. Young, *J. Appl. Chem.*, **17**, 243 (1967).
- (11) See, for example, (a) P. Gaubert, *C. R. Acad. Sci.*, **184**, 527 (1927); (b) *ibid.*, **184**, 384 (1927); (c) "Gmelins Handbuch der Anorganischen Chemie", Vol. 68C, 8th ed, Verlag Chemie, Berlin, Germany, 1942, p 264; (d) K. Krogmann and D. Stephan, *Z. Anorg. Allg. Chem.*, **362**, 290 (1968); (e) L. C. Stecker, R. L. Musselman, P. L. Johnson, and J. M. Williams, to be submitted for publication.
- (12) S. Yamada, *Bull. Chem. Soc. Jpn.*, **24** (3), 125 (1951).
- (13) M. L. Moreau-Colin, *Struct. Bonding (Berlin)*, **10**, 189 (1972).
- (14) P. Weselsky, *J. Prac. Chem.*, **69**, 279 (1856); ref 11c, p 271.
- (15) Research participant sponsored by the Argonne Center for Educational Affairs from Coe College, Cedar Rapids, Iowa.
- (16) In visible light small needle crystals of this material appear red when viewed along the needle axis and green when light is reflected from the faces parallel to the needle axis.

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Synthesis and Binding Characteristics of Macrocyclic Polyethers Containing Convergent Methoxyaryl or Phenolic Groups¹

Sir:

Convergence of binding sites and of potential catalytic functional groups is a problem central to the design and synthesis of nonpeptide catalysts that might imitate enzymes. Hydroxyl groups of phenols are found in active sites of enzymes (e.g., carboxypeptidase)² and play important roles in organization of ionophores that wrap around metal ions (e.g., antibiotic X-537A).³ Phenolic ether groups as parts of crown ether rings are fairly good ligands for the alkali metal ions,^{4a} and the crown ethers have been widely used as lipophilizers of salts and anion activators.^{5a} Association constants of the simple crown ethers with alkali metal ions have been measured.^{5b,c} In prior work we have reported the synthesis of macrocyclic polyethers containing inward-turning furan,^{6a} pyridyl,^{6b} and phenyl-