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# Platinum Bronzes. IV.[1] Preparation, Crystal Chemistry, and Physical Properties

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The syntheses of several ternary platinum oxides are reported. The Na and Cd bronzes $Na_xPt_3O_4$ and $Cd_xPt_3O_4$ as well as the bronze-like $CaPt_2O_4$ were prepared in powder form under atmospheric pressure. The existence of $Pt_3O_4$ is discussed. Syntheses for $Cd_xPt_3O_6$ and a poorly defined new simple oxide of platinum with stoichiometry $Pt_5O_6$ are given. The stability of these various oxides is discussed and their lattice parameters are given. The crystal chemistry of these oxides is systematized using stability fields for the platinum bronzes and for $A_3BX_4$ compounds. The close structural relationship between the bronzes and $Ag_3PO_4$ and $Ag_3AsO_4$ is discussed. Photoelectron spectroscopic, magnetic susceptibility, and electrical conductivity data for the bronzes and various other platinum oxides are reported. From these data it is concluded that most bronzes are metallic oxides and a qualitative one-electron energy-band scheme is given explaining this metallic character. The nonexistence of $CaPt_3O_4$ is discussed in terms of both this scheme and thermodynamics. The tendency of the bronzes to incorporate large quantities of foreign cations is explained in terms of the cage-like bronze structure.

## Introduction

As stated in the previous papers in this series[1] one of the main reasons for the study of platinum oxides arises from the use of platinum as a supposedly inert material in high-temperature chemistry. Because most high-temperature reactions and processes are studied under normal-pressure conditions, those oxides that form under atmospheric pressure are of special importance. Interest in platinum oxides is by no means new. Ever since the early studies of Jorgensen and Wohler[2] these oxides have been a matter of controversy. Several oxides have been reported and forgotten because their existence could not be verified.[3] Even today the electrochemical literature abounds with electrode reactions involving "PtO," a compound whose existence is at least doubtful.[4] The catalytic activity of some oxides of this noble metal provides a further impetus for investigating their existence, formation, and stability.

This last point, the stability of the noble metal oxides, was stressed by Shannon and coworkers in their report on $ABO_2$ delafossite-type noble metal oxides.[5] Although new thermodynamic data for PdO, $PtO_2$, and "$Pt_3O_4$" (see below) tend to ascribe a higher stability to these oxides than was previously accepted ($\Delta G_f^\circ = -40, -75$, and $-88$ kcal/mol, respectively, for 2 PdO,[6a] $PtO_2$,[6b] and $^1/_2$ $Pt_3O_4$[6c]), their contention that ternary noble metal oxides (especially with a transition metal) are difficult to prepare remains valid. Yet most platinum-metal bronzes, which are ternary oxides of general formula $A_3B_xO_4$, where B is commonly a group I or II cation, $0 < x < 1$, and A is Pt or Pd, can be prepared at atmospheric pressure in powder form. We have thus concentrated our studies on the platinum bronzes. Earlier we reported the crystal structure of $Ni_{0.25}Pt_3O_4$, as derived from single-crystal X-ray diffraction data.[1a] A neutron- and X-ray powder diffraction study showed $Cd_{0.3}Pt_3O_4$ to have essentially the same structure, while that of $CaPt_2O_4$ turns out to be closely related.[1b] Also the catalytic activity of some platinum bronzes and other platinum oxides has been reported.[1c] Both the structural and catalytic data show that the bronzes are an unusual family of metal oxides. The present paper deals with the preparation of $Cd_xPt_3O_4$, $CaPt_2O_4$, $Na_xPt_3O_4$, and related platinum oxides. The crystal chemistry of the platinum and palladium bronzes and the silver "pseudobronzes" $Ag_3PO_4$ and $Ag_3AsO_4$ will be discussed. In the second part of this paper the results of X-ray photoelectron spectroscopic (XPS = XPES = ESCA), magnetic susceptibility, and electrical conductivity studies of the bronzes are presented and interpreted in terms of the bronze structure and a qualitative energy-band scheme.

## Experimental Section

**Reagents.** The starting materials used were all reagent grade or better. The Pt-containing starting materials were prepared from either Pt sponge or $K_2PtCl_4$. $(NH_4)_2PtCl_6$ and $H_2PtCl_6 \cdot 6H_2O$ were prepared according to well-known literature methods.[7] For the preparation of Pt black we found the method of Tetenyi and Babernics[8] to give better results than that of Brauer.[9] Contrary to what has been reported by Scheer for $NaPt_3O_4$, we found that drying

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[1] (a) Part I: D. Cahen, J. A. Ibers, and R. D. Shannon, *Inorg. Chem.*, 11, 2311 (1972). (b) Part II: D. Cahen, J. A. Ibers, and M. M. Muller, *ibid.*, 13, 110 (1974). (c) Part III: D. Cahen and J. A. Ibers, *J. Catal.*, 34, 369 (1973).

[2] (a) S. M. Jorgensen, *J. Prakt. Chem.*, 16, 344 (1877); (b) L. Wohler, *Z. Anorg. Chem.*, 40, 450 (1904).

[3] See, for example, O. Muller and R. Roy, *J. Less-Common Metals*, 16, 129 (1968), and references therein.

[4] For a critical review of Pt surface oxides see H. Augerstein-Kozlowska, *et al.*, *J. Electroanal. Chem.*, 43, 9 (1973).

[5] R. D. Shannon, D. B. Rogers, and C. T. Prewitt, *Inorg. Chem.*, 10, 713 (1971).

[6] (a) H. Kleykamp, *Z. Phys. Chem.* (*Frankfurt am Main*), 71, 142 (1970); (b) A. M. Sukhotin, E. A. Gankin, and B. Ya. Shal'man, *J. Appl. Chem. USSR*, 45, 1542 (1972); (c) *ibid.*, 45, 1548 (1972).

[7] (a) G. B. Kauffman, *Inorg. Syn.*, 9, 182 (1967); (b) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1965, p 1569.

[8] P. Tetenyi and L. Babernics, *Acta Chim.* (*Budapest*), 35, 419 (1963).

[9] Reference 7b, p 1562.

the $O_2$ or use of high-purity $O_2$ gas did not influence the reaction.[10]

**Apparatus and Procedures.** All reactions, except for the preparation of the sodium bronzes, were carried out in a Marshall vertical-tube furnace, equipped with a Leeds and Northrup temperature control. A given sample was loaded in a Coors AD 99% recrystallized high-alumina crucible; the crucible was placed in a quartz tube fitted with a gas inlet and outlet and a Pt–Pt–10% Rh thermocouple. The temperature was controlled within 5°. Under no conditions did we observe any chemical attack on the crucible. The thermocouple, however, suffered severe attack and had to be replaced several times.

The preparation of the Na bronzes from "$PtO_2 \cdot H_2O$" or $Na_2CO_3$ and Pt black was carried out in air in a Lindberg SB single-zone furnace. The preparation according to Adams (see below) was carried out in a Pt crucible on a standard laboratory burner.

The X-ray photoelectron spectra were obtained with a PDP8/S computer interfaced on an AEI/ES 100B spectrometer as described elsewhere.[11]

Static magnetic susceptibility measurements were made on a Faraday balance composed of a Cahn electrobalance and Varian electromagnet. The balance was calibrated with NBS standard weights and the magnetic field gradient was mapped out using a gaussmeter. $HgCo(SCN)_4$ was used as a standard ($\chi_g = 16.35 \times 10^{-6}$ emu/g). The field strength could be varied from 3 to 12 kG. Measurements were made between 77 and 300°K. The magnetic field was intermittently pulsed on and off in order to eliminate errors resulting from a zero drift of the balance. The usual sample weight was 15 mg.

Electrical conductivity measurements were made on pellets pressed at ~100,000 psi, with the four-probe van der Pauw technique, as described elsewhere.[12] Both dc and ac ($10^2$–$2 \times 10^4$ Hz) resistivities were measured between 77°K and room temperature. Some difficulties were encountered in the pressing of pellets of the bronzes for conductivity studies. Simply grinding the powders and pressing at pressures between 50,000 and 150,000 psi invariably resulted in cracked pellets. Good pellets could be obtained by adding several drops of water to ~1 g of the ground powder. The pressed pellet was subsequently heated at ~125° for several hours. Such pellets had densities between 75 and 85% of the theoretical value. The complications that arose in the pressing of pellets are probably related to the extreme hardness of the bronzes. Powdered bronzes are harder than agate, as is illustrated by the scratches on an agate mortar after grinding. Because of the low thermal stability of the oxides that were investigated, the pellets could *not* be properly sintered. Therefore all measurements were made on the pellets as pressed.

**Characterization.** Because of their simple cubic structure[1a,b] the bronzes are easily identified by X-ray diffraction. All the products were investigated by X-ray powder diffraction using either a NORELCO diffractometer or a 114-mm Debye–Scherrer camera. Lattice parameters reported in this paper were obtained from weighted, least-squares analyses of the *d* values from the diffraction spectra. Because nearly every reaction yielded metallic Pt as a by-product, the Pt lines served as standards in most cases. Several diffraction spectra were calibrated with TlCl as an internal standard as well. Elemental analyses were performed by Meade Analytical Laboratories, Galbraith Laboratories, and Battelle Laboratories. Rough qualitative analyses were performed by the ESCA technique.

**Purification.** The bronzes are not attacked by boiling aqua regia and this property provides an easy method of purification. The crude products were first boiled in $H_2O$ and $NH_4Cl$ solution, filtered off, and boiled in aqua regia under vigorous stirring. This way all but traces of metallic Pt were removed. All Pt could be removed by repeating this aqua regia treatment. In no instance did we find evidence for a leaching of the counterion out of the bronze as has been reported for some palladium bronzes.[13] All measurements were made on samples free of metallic Pt, as judged by X-ray powder diffraction and ESCA.

## Preparation and Crystal Chemistry

**Syntheses.** The sodium as well as the cadmium and calcium bronzes could be prepared by a simple solid-state reaction where the reactants were intimately mixed together and heated in $O_2$ or air. Neither the use of a flux (to carry out the reaction in a melt) nor the participation of a transport agent such as $I_2$ (for a chemical transport reaction) yielded reasonable amounts of bronze-like products. The only exception is the preparation of $Na_xPt_3O_4$ in a $NaNO_3$ melt.

Table I shows some of the compounds that were synthesized and the reactants and conditions used. These syntheses will now be discussed in some detail.

**I, Cd.** With the preparation of a cadmium–platinum bronze $Cd_xPt_3O_4$, there are now three-well-defined oxides known in the Cd-Pt-O system. Muller and Roy synthesized $Cd_2PtO_4$ under relatively high $O_2$ pressure (150 atm).[14] Shannon and Hoekstra, *et al.*, reported the synthesis of $Cd_xPt_3O_6$ using very high pressures (40 kbars).[15] We found that $CdPt_3O_6$ can be prepared under 1 atm of oxygen at moderate temperatures. The temperatures at which $Cd_xPt_3O_6$ formation takes place lie very close to the formation temperature of $Cd_xPt_3O_4$. If the reaction temperature is below 500°, no reaction takes place. Heating the reactants for 1 week between 500 and 550° gives nearly stoichiometric $CdPt_3O_4$ in very low yields. The amount of Cd incorporated in the bronze seems to decrease with increasing reaction temperature. Between 550 and 590° $Cd_xPt_3O_4$ is formed with $x < 1$. If the reaction temperature is $>590°$, $Cd_xPt_3O_6$ is the only product besides Pt metal. Above 800° only Pt metal is formed. It is possible to use Pt black as the source of platinum instead of $(NH_4)_2PtCl_6$, but generally lower yields of bronzes were obtained. No $Cd_2PtO_4$ was obtained as a major product under any reaction conditions, but ESCA and X-ray diffraction experiments suggest that a thin layer of $Cd_2PtO_4$ is present on the Cd bronze.

**II, III, Na.** The relation between "$PtO_2 \cdot H_2O$" and $Na_xPt_3O_4$ has been discussed elsewhere.[1c] Reaction II is essentially the procedure used by Scheer.[10] Excess $Na_2CO_3$ is essential. Contrary to the report by Waser and McClanahan[16] we have found $NaPt_3O_4$ to be stable in air at room temperature over a period of 3 years. The Na bronze is decomposed into Pt if allowed to react with $H_2$ at room temperature, presumably because of the reaction between $H_2$ and adsorbed $O_2$, which causes the oxide to heat up above its decomposition temperature (~550°).

When the reaction is carried out at liquid $N_2$ temperature only very minor decomposition into Pt metal is observed, and after all the adsorbed $O_2$ has reacted, the bronze is stable toward $H_2$ even at room temperatures. If reaction II is allowed to go for several weeks, very small $NaPt_3O_4$ crystals (blue-black) are formed.

**IV, Ca.** The formation of $CaPt_2O_4$ proceeds quantitatively if the reactants are mixed well. The reaction equation can be written as

$$2(NH_4)_2PtCl_6 + 4CaCO_3 \rightarrow CaPt_2O_4 + 3CaCl_2 + \\ 4NH_4Cl(\text{sublimes}) + 4CO_2 + Cl_2$$

We confirm Post's findings that $CaPt_2O_4$ is formed between 800 and 900°.[17] With $CaCl_2 \cdot H_2O$ as a flux it is possible to prepare the Ca bronze, but the yield is much smaller and several other calcium platinum oxides are formed, including a

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(10) J. J. Scheer, Thesis, Leyden, 1956. See also J. J. Scheer, A. E. van Arkel, and R. D. Heyding, *Can. J. Chem.*, 33, 683 (1955).

(11) (a) D. Cahen and J. E. Lester, *Chem. Phys. Lett.*, 18, 108 (1973); (b) R. Bastasz, D. Cahen, J. E. Lester, and J. Rajaram, *ibid.*, 22, 489 (1973).

(12) D. Cahen, J. R. Hahn, and J. R. Anderson, *Rev. Sci. Instrum.*, 44, 2567 (1973).

(13) O. Muller and R. Roy, *Advan. Chem. Ser.*, No. 98, 28 (1971).

(14) O. Muller and R. Roy, *J. Less-Common Metals*, 20, 161 (1970).

(15) (a) R. D. Shannon, U. S. Patent 3,663,181 (1972); (b) H. R. Hoekstra, S. Siegel, and F. X. Gallagher, *Advan. Chem. Ser.*, No. 98, 39 (1971).

(16) J. Waser and E. D. McClanahan, *J. Chem. Phys.*, 19, 413 (1951).

(17) B. Post, private communication.

**Table I.** Sample Preparations of Platinum Bronzes[a]

| Reacn no. | Reactants | Temp, °C | Time | Atm | Method | Major products | Color | Analysis |
|---|---|---|---|---|---|---|---|---|
| I | $2CdCO_3 + (NH_4)_2PtCl_6$ | 580 | 1 week | $O_2$ | ss | $Cd_xPt_3O_4$, $Cd_xPt_3O_6$, Pt | Gray-black | ea, X, E |
| II | $Na_2CO_3$ + Pt(black) | 525 | 1 week | Air, $O_2$ | ss, pellet | $NaPt_3O_4$, Pt | Pitch black | ea, X, E, ms |
| III | $NaNO_3$(excess) + $H_2PtCl_6 \cdot 6H_2O + H_2O$ | ~700 | 30 min | Air | Flux, boil | $Na_xPt_3O_4$, $\alpha$-$PtO_2 \cdot xH_2O$, Pt | Gray-black | ea, X, E, ms |
| IV | $2CaCO_3 + (NH_4)_2PtCl_6$ | 825 | 2 days | $O_2$ | ss | $CaPt_2O_4$ | Violet | ea, X |
| V | $BaO_2$ + Pt(black) | 590 | 2 days | $O_2$ | ss | $Pt_3O_4$, Pt | Black | ea, X, E |
| VI | $BaO_2 + (NH_4)_2PtCl_6$ | 560 | 1 week | $O_2$ | ss | Pt, "$Pt_5O_6$" | Gray | ea, X, E |

[a] Abbreviations: ss, solid state; ea, elemental analysis; X, X-ray diffraction; E, ESCA; ms, mass spectrum.

cubic white phase of unknown stoichiometry and rhombohedral $Ca_4PtO_6$.[18]

**V, VI, Ba.** We were unable to form a platinum bronze containing Ba, probably because of the large size of the $Ba^{2+}$ ions. However, by using $BaO_2$ as a starting material some interesting products were obtained. Under the conditions of reaction V one of the products had a diffraction pattern corresponding to the general bronze structure. Spectroscopic analysis showed the presence of a very small amount ($x < 0.1$) of Pb. (Pb is present as an impurity in $BaO_2$.) As can be seen from Table II and Figure 1 the lattice parameter of this phase corresponds closely to that of $Pt_3O_4$.[3] One of the products of reaction VI is tentatively formulated as $Pt_5O_6$ on the basis of the results of an elemental analysis. No elements other than Pt and O could be detected by ESCA. The phase is resistant to attack by acids and aqua regia. (See Appendix.)

**Results of Syntheses.** Table II shows some structural data for the bronzes known today. For the sake of uniformity the conventional formulation has been turned around. By using the $A_3BO_4$ notation the similarity between the bronzes and silver phosphate and arsenate becomes more obvious. Included in the table is $CaPt_2O_4$, a tetragonally distorted two-dimensional analog of the bronzes.[1b]

The lattice constants listed are those at room temperature. We found only very minor differences between the lattice parameter of a quenched and an annealed sample of $Na_xPt_3O_4$ (less than 0.01 Å). Figure 1 shows a plot of the unit cell volume of the platinum bronzes *vs.* the ionic radius of the counterion B. (The ionic radii in this paper are taken from the compilations by Shannon and Prewitt.[19]) In the terminology of Shannon and Prewitt this is a type I stability field.[20] This plot is used here mainly to point out how the lattice parameter of a bronze might give some indication about the magnitude of the parameter $x$. Two points are shown for $Pt_3O_4$, the lowest one corresponding to the high-pressure phase prepared by Muller and Roy.[3] How far their phase is truly $Pt_3O_4$, free of counterions, is open to question. Reaction V (Table I) illustrates that even very small amounts of impurities can be incorporated into the bronze structure. Furthermore a sample of $Na_xPt_3O_4$ was shown, by broad-line nmr, to contain H in addition to Na. The presence of $H_2O$ in the bronzes is ruled out by the absence of any O-H stretching band in the ir spectrum, but it is possible that the $Pt_3O_4$ phases are actually $H_xPt_3O_4$. The higher point corresponds to the product of reaction V (Table I).

Both the Ni[1a] and the Mg[13] bronzes were prepared under high pressures while all the remaining bronzes were synthesized under atmospheric pressure. Figure 2 shows the crystal structures of $CaPt_2O_4$ and that of $Cd_{0.3}Pt_3O_4$ (the general bronze structure).

**Table II.** Cell Dimensions, Interatomic Distances, and Ionic Radii for $A_3BO_4$ Bronzes

| Compd[a] | $a_0$, Å | $r_B$, Å | B–O,[b] Å | A–A,[b] Å | $x$ |
|---|---|---|---|---|---|
| $Pt_3\square O_4$[c] | 5.585 | | 2.418 | 2.792 | |
| $Pt_3\square O_4$[d] | 5.592 | | 2.421 | 2.796 | |
| $Pt_3Mg_xO_4$[e] | 5.621 | 0.89 | 2.434 | 2.810 | <0.2 |
| $Pt_3Ni_{0.25}O_4$[f] | 5.61 | 0.78[g] | 2.43 | 2.80 | ~0.25 |
| $Pt_3Na_xO_4$[d] | 5.596 | 1.16 | 2.423 | 2.798 | ~0.1 |
| $Pt_3Na_xO_4$[h] | 5.66 | 1.16 | 2.45 | 2.83 | ? |
| $Pt_3Na_xO_4$[i,j] | 5.689 | 1.16 | 2.463 | 2.844 | >0.9 |
| $Pt_3Cd_xO_4$[d] | 5.639 | 1.07 | 2.442 | 2.820 | ~0.2 |
| $Pt_3Cd_xO_4$[k] | 5.642 | 1.07 | 2.443 | 2.821 | ~0.3 |
| $Pt_3Cd_xO_4$[d] | 5.688 | 1.07 | 2.463 | 2.844 | >0.9 |
| $Pt_2\square Ca_xO_4$[k] | 5.779[l] | 1.12 | 2.481 | 2.79 | 1 |
| | 5.599 (= $c_0$) | | | 2.99 | |
| $Pd_3Na_xO_4$[i] | 5.64 | 1.16 | 2.44 | 2.82 | 1 |
| $Pd_3Cd_xO_4$[e] | 5.742 | 1.07 | 2.486 | 2.871 | 1 |
| $Pd_3Ca_xO_4$[e] | 5.747 | 1.12 | 2.445 | 2.874 | 1 |
| $Pd_3Sr_xO_4$ | 5.826 | 1.25 | 2.523 | 2.913 | 1 |
| $Ag_3PO_4$[m] | 6.013 | 0.3[g] | 1.7[g] | 3.006 | 1 |
| $Ag_3AsO_4$[m] | 6.133 | 0.6[g] | 2.0[g] | 3.065 | 1 |

[a] All the Pt and Pd bronzes crystallize in space group $O_h{}^3$-$Pm3n$ and the Ag "pseudobronzes" crystallize in space group $T_d{}^4$-$P\bar{4}3n$. [b] Calculated for the idealized structures. [c] Reference 3. [d] Present work. [e] Reference 13. [f] Reference 1a. [g] Estimated. [h] A. M. Sukhotin, E. A. Gankin, Yu. D. Kondrashov, Yu. A. Omel'chenko, and B. Ya. Shalman, *Russ. J. Inorg. Chem.*, 16, 1690 (1971). [i] Reference 10. [j] Reference 16. [k] Reference 1b. [l] Tetragonally distorted. [m] R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience, New York, N. Y., 1965, p 152.

**Discussion.** The very narrow temperature regions in which formation of the bronzes is possible suggests that these phases have a very low stability or may be even metastable under 1 atm of oxygen, with respect to transformation into other oxides or into Pt metal. The sodium bronze, for example, is formed only between 500 and 550°. Above this temperature $Na_2PtO_3$ is formed.[10] A similar situation exists for the Cd bronze as was described above. The Ca bronze is stable only over the 100° interval between 800 and 900°; above 900° only Pt metal is obtained.[17] This low stability probably accounts for the difficulty encountered in the preparation of these materials. However, once formed they are remarkably stable, as long as they are not heated above their formation temperature. It is this last aspect that is of practical importance as it indicates certain conditions under which platinum *cannot* be used as an inert material. The bronzes seem to be best stabilized by group I or II cations as long as certain size requirements are met. For the platinum bronzes the counterion (B) should probably not have an ionic radius exceeding 1.2 Å, while for the Pd bronzes the maximum radius seems to be 1.3 Å as can be seen from the fact that no Ba–Pd or Sr–Pt bronze has been prepared, even under high pressures.

Sukhotin and coworkers measured the free energy of for-

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(18) R. Czaya, *Z. Anorg. Allg. Chem.*, 375, 61 (1970).

(19) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969); 26, 1046 (1970).

(20) R. D. Shannon and C. T. Prewitt, *J. Inorg. Nucl. Chem.*, 32, 1427 (1970).

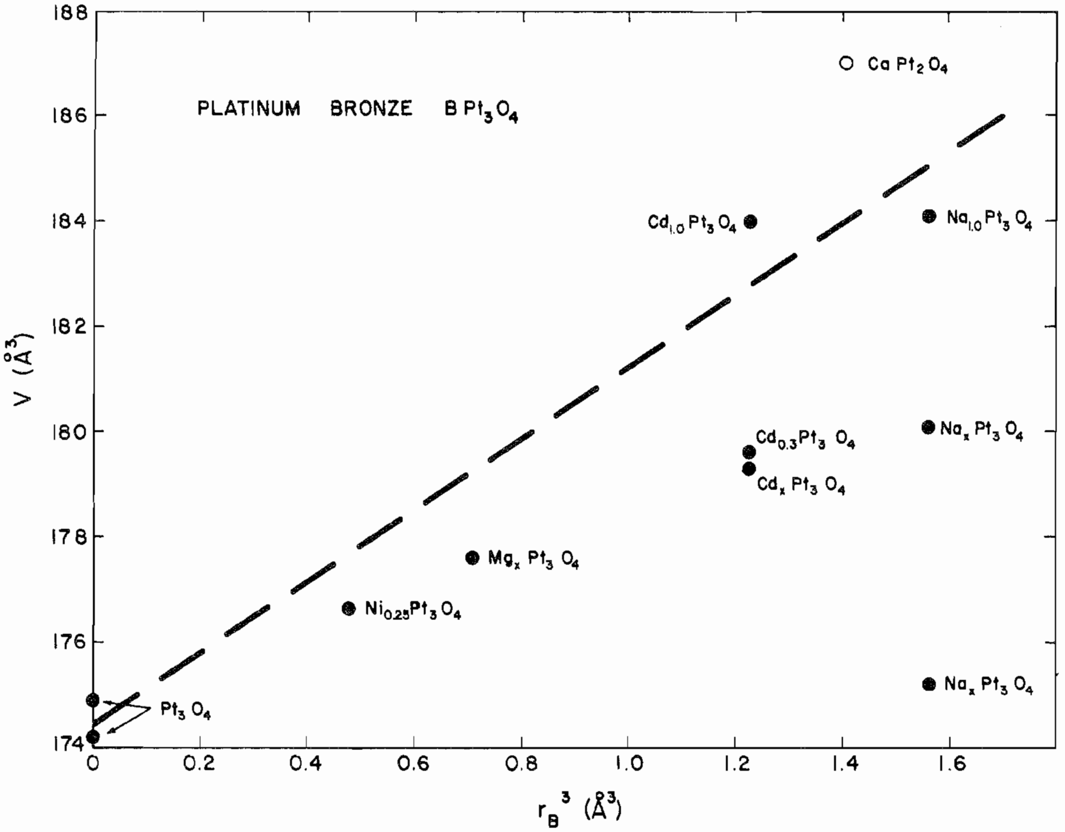
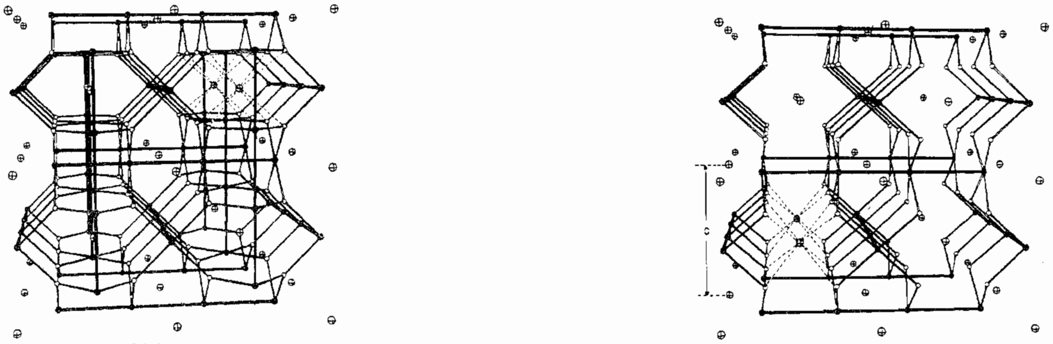


**Figure 1.** Stability field of platinum bronzes (plot of $r_B{}^3$ *vs.* unit cell volume). Compounds which fall below the dotted line will probably be nonstoichiometric.



CD 0.3 PT3 O4

CA PT2 O4

**Figure 2.** Crystal structures of $Cd_{0.3}Pt_3O_4$ (general bronze structure) and $CaPt_2O_4$ (from ref 1b). The oxygen and platinum atoms are drawn as open and solid circles, respectively. The coordination of oxygen around the counterions is shown in the upper right-hand corner (for $Cd_{0.3}$-$Pt_3O_4$) and in the lower left-hand corner (for $CaPt_2O_4$).

mation of both "$PtO_2$" and "$Pt_3O_4$" by electrochemical methods.[6b,c] Unfortunately their methods of preparation make it very likely that their "$PtO_2$" phase was a mixture of $\alpha$-$PtO_2 \cdot xH_2O$ and $Na_xPt_3O_4$, while "$Pt_3O_4$" was most probably $Na_xPt_3O_4$.[1c] Nevertheless on the basis of the values they obtained (−75 kcal/mol for "$PtO_2$" and −59 kcal/mol per Pt for "$Pt_3O_4$") the formation of these oxides can be understood.

It is not obvious why $CaPt_2O_4$ rather than $CaPt_3O_4$ is formed and why this formation takes place at a much higher temperature than for the other platinum bronzes. One possible clue for this behavior might be found in the exceptionally low free energy of formation of CaO as compared with that of other oxides. Ellingham diagrams[21] (plots of $\Delta G_f{}^\circ$ *vs.* $T$) illustrate this very markedly. However, such diagrams show also that MgO has only a slightly less negative $\Delta G_f{}^\circ$ than CaO. A Mg-Pt bronze has been prepared but only under high oxygen pressure. It follows then that if indeed the stability of the oxide of the counterion plays a role in the nonformation and formation temperature of the bronzes, it should be possible to prepare $Ca_xPt_3O_4$ under high oxygen pressures. But this line of argument does not explain why Ca forms a two-dimensional bronze analog under atmospheric pressures (and Mg does not). A possible electronic explanation will be given below.

The ideal stoichiometric ratio of counterion, platinum, and oxygen in the bronzes would be 1:3:4. Only if the counterion is divalent and the $x$ parameter (in $A_3B_xO_4$) is 1, can we assign a "normal" formal oxidation state to platinum, namely, 2+. But the bronze structure contains infinite chains of metallic bonded platinum atoms and because of this metallic

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[21] See, for example, J. F. Eliot and M. Gleiser, "Thermochemistry for Steelmaking," Vol. I, Addison-Wesley, Reading, Mass., 1960, p 214.

bonding the concept of a formal oxidation state loses much of its meaning. Therefore we feel that the fact that Pt has an oxidation state of 2.3+ or 3+ in certain bronzes is more a matter of arithmetic than of chemistry. It seems that the platinum chains act as electron sinks to which electrons can be added or from which they can be taken. A further complication is encountered when we look at the experimental O:Pt ratio. In nearly all the bronzes analyzed we found this ratio to be lower than 1.33. Although analyses for oxygen are generally less accurate than those for Pt or Na, the fact that the O:Pt ratio consistently comes out below 1.33:1 suggests the presence of Pt interstitials, O vacancies, or impurity anions on the oxygen sites. Sukhotin, *et al.*,[22] put forward these possibilities in the light of the O:Pt ratio of 1.18:1 that they obtained for "$Pt_3O_4$."

Figure 3 shows a type II stability field[20] (a plot of $r_A$ *vs.* $r_B$) for compounds with the $A_3BX_4$ stoichiometry. This stoichiometry is rarely found in oxides or sulfides. For the sake of completeness the $A_3BS_4$ compounds have been included. Only four structure types are known that give rise to the $A_3BO_4$ stoichiometry. The $Li_3PO_4$ and $Ba_3NiO_4$ crystal structures are completely unrelated to the third type, the bronze structure, or the fourth one, the $Ag_3PO_4$ structure. $Ag_3PO_4$ and $Ag_3AsO_4$ have a structure closely related to that of the bronzes.[23] This relation is illustrated in Figure 4. By displacing the oxygen atoms in the bronze structure slightly from their symmetric ($^1/_4$, $^1/_4$, $^1/_4$) position a tetrahedral coordination of oxygen around the phosphorus or arsenic atom is obtained.

Muller, *et al.*, reported the preparation of $Na_{0.5}Au_2O_3$.[24] On the basis of their X-ray diffraction spectra they proposed a defect bronze structure for this compound, which could then be written as $Na_{2/3}\square_{1/3}(Au_{8/3}\square_{1/3})O_4$. As can be seen from Figure 3, a sodium-gold bronze would lie very close to the bronze stability field.

Because of the variation in coordination number of the ions in different $A_3BX_4$ structures, Figure 3 should not be interpreted as an exact classification but rather as a rough guide for future syntheses.

## Physical Properties

**Results. I. XPES.** Figure 5 shows three typical X-ray photoelectron spectra of the Pt 4f core electron levels. The Pt photoelectron spectrum of $Cd_xPt_3O_6$ is of interest because of the presence of two kinds of Pt atoms in this compound[15a] (See Figure 6). The resulting spectrum is a triplet which can be decomposed into two doublets. The binding energies of the doublets correspond to $Pt^{2+}$ and $Pt^{4+}$. The intensity ratio of the doublets is approximately 1:2, which agrees with the formulation $Cd_xPt^{2+}Pt^{4+}{}_2O_6$ as derived from structural data. The experimental and deconvoluted spectra of $Cd_xPt_3O_6$ are shown in Figure 7a. The spectrum of the Cd bronze is somewhat puzzling at first glance. In order to explain the observation of a triplet (see Figure 7b) instead of the expected doublet, it should be borne in mind that XPES is essentially a surface technique. It is generally accepted that only electrons from the top 20-30 Å of the sample can escape. Therefore the spectrum is not necessarily representative of the bulk of the material under investigation. If the surface of the sample is contaminated, such contamination

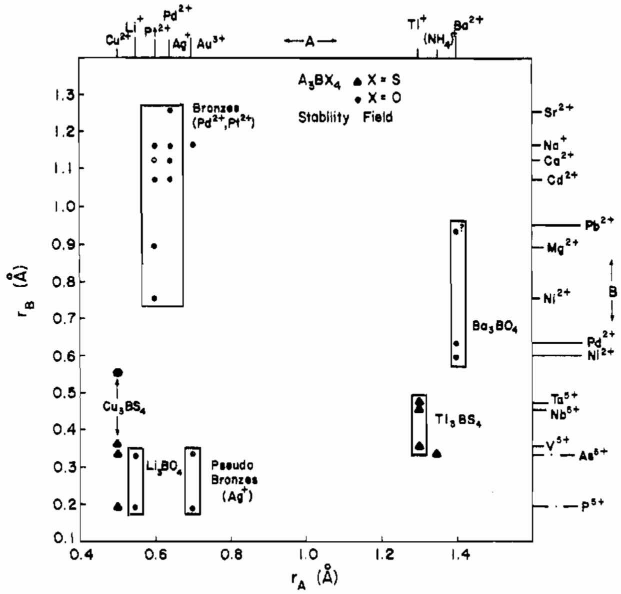

**Figure 3.** Stability fields for $A_3BX_4$ compounds (plot of $r_A$ *vs.* $r_B$).

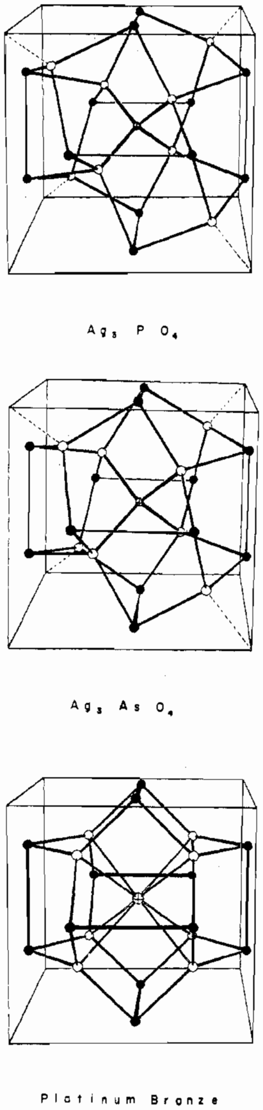

**Figure 4.** Comparison of the unit cell contents of the "pseudobronzes" $Ag_3PO_4$ and $Ag_3AsO_4$ (top and center) with that of the platinum bronzes (bottom). The silver and platinum atoms are drawn as closed circles and the oxygen atoms as open ones.

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[22] A. M. Sukhotin, E. A. Gankin, Yu. D. Kondrashov, Yu. A. Omel'chenko, and B. Ya. Shal'man, *Russ. J. Inorg. Chem.*, 16, 1690 (1971).

[23] R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience, New York, N. Y., 1965, p 152.

[24] O. Muller, R. E. Newnham, and R. Roy, *J. Inorg. Nucl. Chem.*, 31, 2966 (1969).

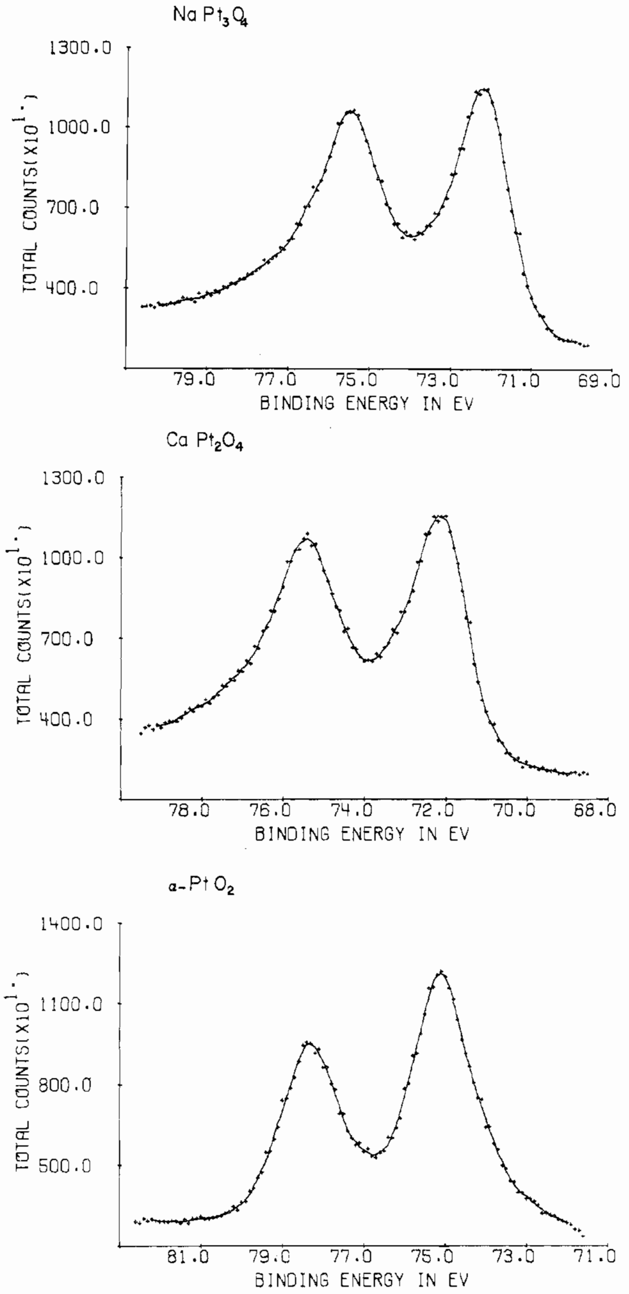

**Figure 5.** X-Ray photoelectron spectra of the Pt 4f levels for $NaPt_3O_4$ (top), $CaPt_2O_4$ (center), and $\alpha$-$PtO_2$ (bottom). The spectra are fitted to a nine-term polynomial.

might well show up in the spectrum. Such is often the case if pure metals are studied.[25] Here we are dealing with a metal oxide and the possibility exists that the surface oxide is different from the bulk. We believe this to be the case for $Cd_xPt_3O_4$ and base this on two pieces of evidence. (a) The X-ray powder pattern of the bronze shows two very weak peaks which cannot be ascribed to the simple bronze structure while they do correspond to the strongest reflections in the reported $Cd_2PtO_4$ powder pattern.[14] (b) When the Cd bronze sample was bombarded for 10–20 min with a beam of Ar ions ("etching") a spectrum was obtained that looked rather similar to that of the other bronzes. (See Figure 7b.) Thus if we assume that two kinds of Pt were present initially (as for $Cd_xPt_3O_6$), then one kind of Pt is apparently selectively removed by this treatment. Etching of $Cd_xPt_3O_6$ for a similar period of time has little effect on the spectrum but some effect is visible after prolonged etching (1 hr or longer), resulting in a doublet shifted considerably to higher kinetic energies. However at the same time the O 1s peak has all but disappeared.

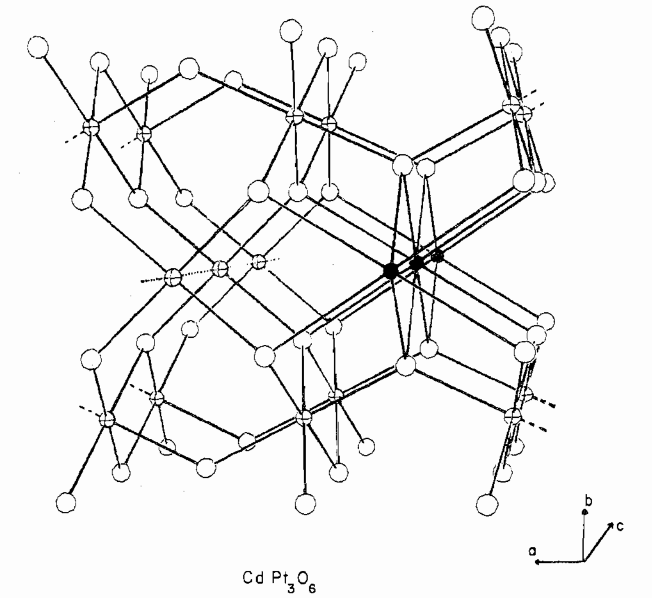

**Figure 6.** Structure of $CdPt_3O_6$.[15a] The cadmium and oxygen atoms are drawn as solid and open circles, respectively. The oxygen coordination around $Pt^{2+}$ is square planar, while that around $Pt^{4+}$ is octahedral. The dotted line indicates a weak metal–metal interaction between the divalent platinum atoms.

It is very likely that such prolonged etching leaves layers of oxygen-depleted platinum on the top of the sample. Still it is unlikely that this explains the drastic change that takes place upon etching $Cd_xPt_3O_4$ for a short time. Here the change is probably caused by the removal of a surface oxide. Thus Figure 7b shows essentially a superposition of the spectrum of $Cd_2PtO_4$ on that of $Cd_xPt_3O_4$. No such superposition is observed in the spectra of the other bronzes. Because of the small particle sizes of the bronzes (generally less than 400 mesh) and because we did observe some diffraction peaks even for $Cd_2PtO_4$, it is likely that the diffraction pattern would have shown the presence of a surface oxide layer more than 20 Å deep.

Table III summarizes the core level binding energies of the bronzes and other platinum oxides. Included in the table are $CoPtO_2$, $\alpha$-$PtO_2$, and $Cd_xPt_3O_6$. Prewitt, *et al.*, reported the crystal structure of $CoPtO_2$ and related compounds.[26] They concluded tentatively that Pt has a formal oxidation state of 1+. It is tempting to consider the low binding energy of the Pt 4f electrons in $CoPtO_2$ as evidence for monovalent platinum. However in this compound, as in the bronzes, extensive Pt–Pt bonding is found (Pt–Pt = 2.830 Å) and therefore not too much importance should be attached to the concept of monovalent Pt in this oxide. Pt is linearly coordinated to two oxygen atoms in these oxides, a situation which is different from the square-planar arrangement found in the bronzes. Very similar binding energies for the Pt 4f electrons are found in $CaPt_2O_4$, $NaPt_3O_4$, and $Cd_xPt_3O_4$. This illustrates the breakdown of the concept of a formal oxidation state in the bronzes as discussed before. It seems, then, that the binding energies for Pt in this oxide are influenced mainly by the local environment of the Pt which varies from

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[25] See, for example, K. C. Tripathi and D. T. Clark, *Nature (London), Phys. Sci.*, 241, 162 (1973).

[26] C. T. Prewitt, R. D. Shannon, and D. B. Rogers, *Inorg. Chem.*, 10, 719 (1971).

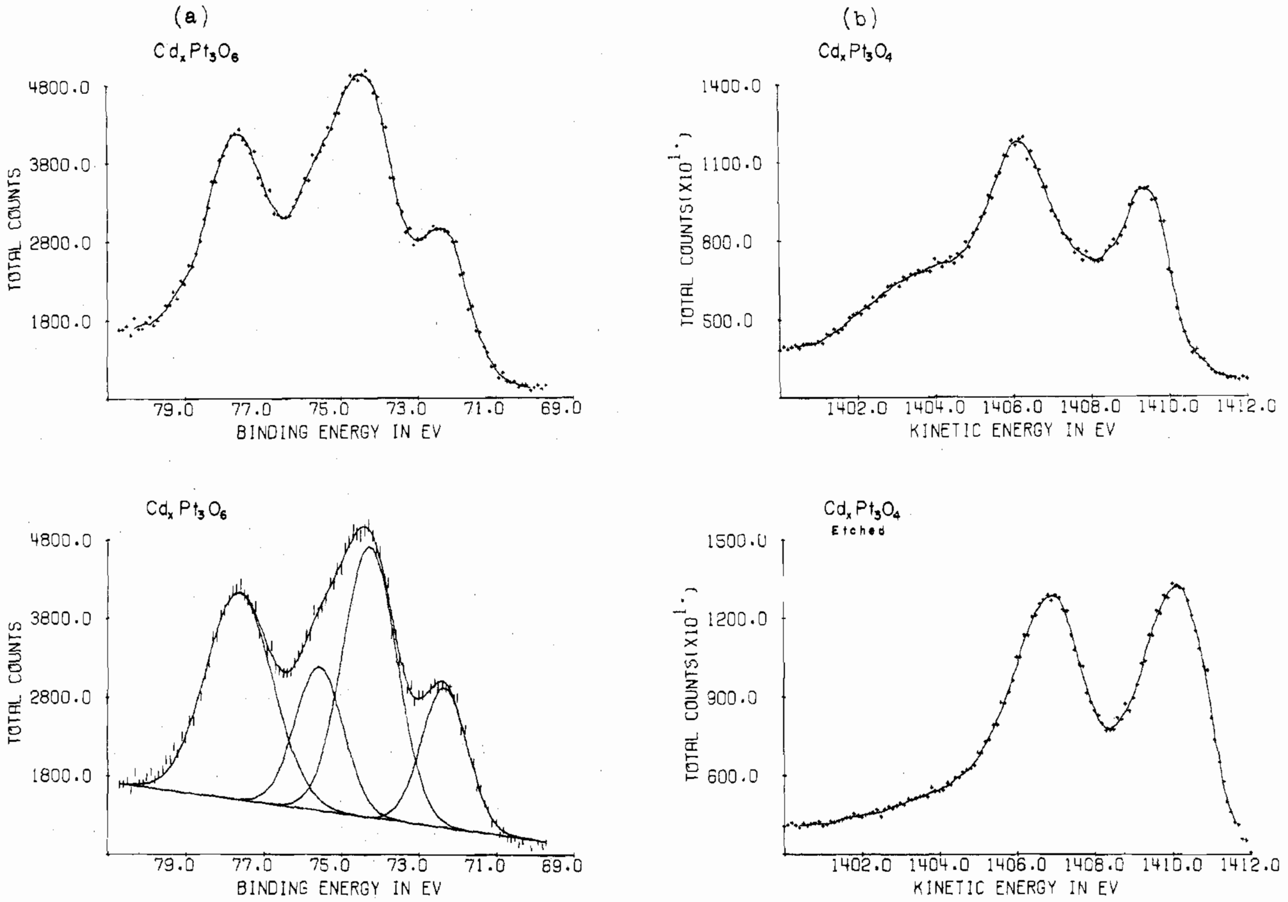

**Figure 7.** (a) X-Ray photoelectron spectrum of the Pt 4f levels of $CdPt_3O_6$ (top) and its deconvolution into two doublets (bottom). (b) X-Ray photoelectron spectrum of the Pt 4f levels of $Cd_{0.3}Pt_3O_4$ before (top) and after (bottom) 10-min etching with an Ar ion beam.

**Table III.** X-Ray Photoelectron Core Level Binding Energies for Pt 4f Electrons (eV)

| Compd | Pt $4f_{5/2}$ | Pt $4f_{7/2}$ | Compd | Pt $4f_{5/2}$ | Pt $4f_{7/2}$ |
|---|---|---|---|---|---|
| Pt metal[a] | 74.5 (1)[b] | 71.2 (1) | $CaPt_2O_4$ | 75.5 (1) | 72.2 (1) |
| $Co^{III}Pt^{I}O_2$ | 75.2 (1) | 71.9 (1) | $\alpha$-$PtO_2$ | 77.6 (2) | 74.4 (2) |
| $NaPt_3O_4$ | 75.6 (1) | 72.2 (1) | $Cd_{0.3}Pt^{2+}Pt^{4+}{}_2O_6$ | 77.5 (1)[c] | 74.2 (1) |
| $Cd_{0.3}Pt_3O_4$ | 75.5 (2) | 72.2 (2) | | 75.4 (1) | 72.2 (1) |

[a] From Y. Baer, P. F. Heden, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, *Phys. Scr.*, 1, 55 (1970). [b] Errors in parentheses. [c] Results from the deconvoluted spectrum.

a linear and square-planar oxygen coordination in $CoPtO_2$ and the bronzes, respectively, to square-planar and octahedral in $Cd_xPt_3O_6$. As discussed below, all the oxides in Table III exhibit relatively high, metal-like conductivity, except for $Cd_xPt_3O_6$ and $\alpha$-$PtO_2$. $\alpha$-$PtO_2$ is by far the poorest conductor in this series and therefore it will be more susceptible to surface charging in an XPES experiment. This charging effect decreases the accuracy with which binding energies can be measured for this oxide and explains the larger estimated error shown in the table.

Figure 8 illustrates the different Na content of $NaPt_3O_4$ and $Na_xPt_3O_4$. Also shown is a typical O 1s spectrum of the bronzes. Apart from the oxide oxygen there is probably some adsorbed oxygen present as well. Physically adsorbed molecular oxygen alone would give rise to a doublet because of its paramagnetism.[27] Combined with the above-described reaction of $H_2$ with Na bronze, an XPES study thus gives additional evidence for the presence of oxygen adsorbed on the surface of the bronzes.

**II. Magnetic Susceptibility.** Table IV lists the magnetic susceptibilities of some bronzes. Diamagnetic corrections were taken from the Landolt-Bornstein tabulations.[28] The Ca, Na, and Cd bronzes all show nearly temperature-independent paramagnetism (TIP). A slight increase of $\chi$ is observed with decreasing temperature. This is probably caused by the presence of paramagnetic impurities and/or adsorbed oxygen. The Cd and Na bronzes show a slight field dependence which could be caused by ferromagnetic impurities. The marked difference in susceptibility between the stoichiometric and sodium-deficient bronzes could be explained by the large quantities of impurities present in $Na_xPt_3O_4$. The temperature dependence of $\chi$ of $Na_xPt_3O_4$ does not fit a simple Curie-Weiss law. Table V compares the impurity levels in the sodium bronzes as determined by spark mass spectrographic analysis. The difference in impurity levels between the two sodium bronzes arises from the different modes of preparation. The solid-state method employed for the preparation of $NaPt_3O_4$ seems to be much cleaner than

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(27) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969, p 56.

(28) Landolt-Bornstein, "Numerical Data and Functional Relationships in Science and Technology," Group II, Vol. 2, Springer-Verlag, Berlin, 1966, pp 1-16.

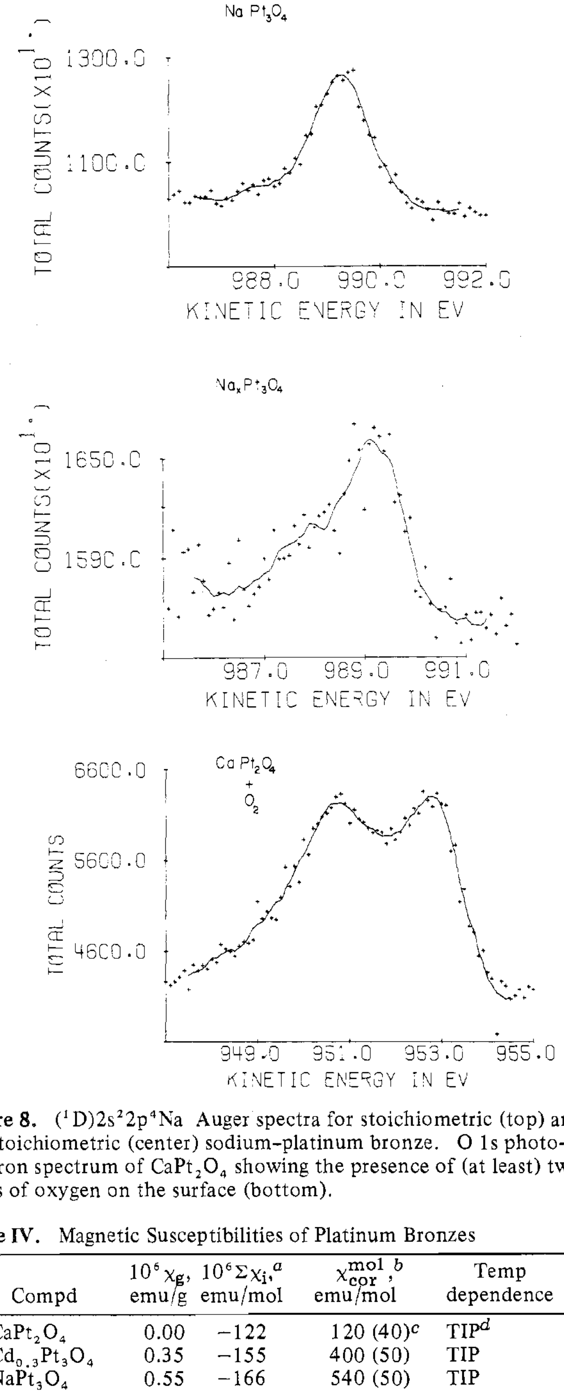

**Figure 8.** ($^1$D)2s$^2$2p$^4$Na Auger spectra for stoichiometric (top) and nonstoichiometric (center) sodium-platinum bronze. O 1s photoelectron spectrum of CaPt$_2$O$_4$ showing the presence of (at least) two kinds of oxygen on the surface (bottom).

**Table IV.** Magnetic Susceptibilities of Platinum Bronzes

| Compd | $10^6\chi_g$, emu/g | $10^6\Sigma\chi_i$,[a] emu/mol | $\chi_{cor}^{mol}$,[b] emu/mol | Temp dependence |
|---|---|---|---|---|
| CaPt$_2$O$_4$ | 0.00 | −122 | 120 (40)[c] | TIP[d] |
| Cd$_{0.3}$Pt$_3$O$_4$ | 0.35 | −155 | 400 (50) | TIP |
| NaPt$_3$O$_4$ | 0.55 | −166 | 540 (50) | TIP |
| Na$_{0.3}$Pt$_3$O$_4$ | 17.50 | −160 | 11,800 (50)<br>(=5.3 $\mu_B$) | ? |
| Ni$_{0.25}$Pt$_3$O$_4$ | 2.20 | −155 | 1,620 (50)<br>(=1.9 $\mu_B$) | Curie-Weiss |
| Cd$_{0.3}$Pt$_3$O$_6$ | 0.60 | −170 | 590 (60) | TIP |

[a] Diamagnetic correction; from ref 28. [b] All values at 290°K. [c] Estimated errors in parentheses. The errors are based on uncertainties in the weighing only and do not include errors in the diamagnetic corrections. [d] Temperature-independent paramagnetism.

**Table V.** Impurities in Sodium-Platinum Bronzes (ppm)[a]

| Element | Na$_{0.3}$-Pt$_3$O$_4$ | NaPt$_3$O$_4$ | Element | Na$_{0.3}$-Pt$_3$O$_4$ | NaPt$_3$O$_4$ |
|---|---|---|---|---|---|
| Ti | 20 | 5 | Ni | 500 | 300 |
| Cr | 200 | 10 | Cu | 20 | 20 |
| Mn | 50 | 5 | Zn | 30 | 20 |
| Fe | 500 | 100 | Pd | 300 | 100 |

[a] Analyses performed by Battelle Laboratories, Columbus, Ohio.

the flux method that we used to prepare Na$_x$Pt$_3$O$_4$.

Earlier we reported that Ni$_{0.25}$Pt$_3$O$_4$ exhibits a nearly temperature-independent paramagnetism.[1a] This result was obtained on a very small amount of Ni bronze crystals. Since then we have repeated this measurement, using a larger quantity of the bronze and a different experimental setup (see above), which increased the sensitivity of the measurements by at least a factor of 5. Such increase is important because all samples except Na$_x$Pt$_3$O$_4$ gave extremely small weight changes in the Faraday balance. The corrected molar susceptibilities partially obscure this because of the large diamagnetic corrections. The high errors on most of the results in Table IV arise from these small weight changes. With the increased sensitivity we observed a Curie-Weiss behavior for the susceptibility of Ni$_{0.25}$Pt$_3$O$_4$. This can be explained if we assume Ni to be present as Ni$^{3+}$ or Ni$^{4+}$ in the high-spin state. Such behavior is not uncommon because the oxide ligand has a ligand field strength comparable with that of water and high spin nickel-aquo complexes are known.[29] It is probably more reasonable to assign the 3+ oxidation state to the nickel ion than the 4+ state, because of the large amount of energy required to stablize Ni$^{4+}$. Table IV also shows that the TIP of Cd$_x$Pt$_3$O$_6$ is of the same order of magnitude as that of the bronzes.

**III. Electrical Conductivity and Valence Band Spectra.** Table VI summarizes the electrical properties of the platinum bronzes and related oxides. The single-crystal data for Na$_x$Pt$_3$O$_4$ are probably correct, even though the material was contaminated with powdered $\beta$-PtO$_2$.[30] The results obtained for NaPt$_3$O$_4$ compaction should be viewed with reservations because of the method used. Our measurements on pressed pellets of the Ca, Cd, and Na bronzes indicate that the conductivity is metallic. This conclusion is based on the room-temperature value of the conductivity and the small temperature dependence between 80 and 300°K, as illustrated in Figure 9 for CaPt$_2$O$_4$. The slightly negative instead of positive temperature coefficient can be explained by the influence of contact resistances between the individual grains in the pellet. Such resistances will exist, because proper sintering of the pellets was impossible. With increasing frequency we see a change in the temperature dependence. This suggests that the observed behavior is not intrinsic.

Cd$_x$Pt$_3$O$_6$ and $\alpha$-PtO$_2$ show semiconducting behavior. Pressed pellets of $\alpha$-PtO$_2$ had a metallic luster but the powder was light brown. X-Ray diffraction showed that the pellet still possessed the $\alpha$ structure and had not been transformed into the $\beta$-phase.[3,15b,30]

The X-ray valence band spectra of the sodium and calcium bronzes, Cd$_x$Pt$_3$O$_6$, and $\alpha$-PtO$_2$ are shown in Figure 10. Figure 11 compares the X-ray and uv valence band spectrum of NaPt$_3$O$_4$. Valence band spectra of metals show appreciable intensity at the Fermi energy, while for insulators none is found above the background noise. Semiconductors generally are intermediate.[31] An exact interpretation of valence band spectra is possible only if accurate band structure calculations or supporting optical and uv absorption spectroscopic data are available. Thus we will not try to interpret the spectra in terms of a band structure but will use them only as supporting evidence for the (non)metallic nature of the compounds under discussion. For such pur-

(29) C. K. Jorgensen, "Modern Aspects of Ligand Field Theory," North-Holland Publishing Co., Amsterdam, 1971, pp 344, 357.

(30) R. D. Shannon, *Solid State Commun.*, **6**, 139 (1968); R. D. Shannon, *ibid.*, **7**, 257 (1969).

(31) Y. Baer, P. F. Heden, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **1**, 55 (1970); K. Hamrin, G. Johansson, U. Gelius, C. Nordling, and K. Siegbahn, *ibid.*, **1**, 277 (1970).

**Table VI.** Electrical Resistivities and Activation Energies for Semiconduction of Some Platinum Oxides

| Compd | Sample form | Method | $\rho$,[a] $\Omega$ cm | Type | $E_a$, eV |
|---|---|---|---|---|---|
| $Ni_{0.25}Pt_3O_4$[b] | Single crystal | 4-probe | $3 \times 10^{-4}$ | Metallic | |
| $CaPt_2O_4$ | Pellet | Ac, *c* | $6 \times 10^{-2}$ | Metallic | |
| $CaPd_3O_4$[d] | Pellet | *c* | 3 | Semiconducting | 0.1 |
| $Cd_{0.3}Pt_3O_4$ | Pellet | Ac, *c* | $10^{-2}$ | Metallic | |
| $NaPt_3O_4$[e] | Powder | Ir drop | $10^4$ | Ionic | |
| $Na_xPt_3O_4$[f] | Crystal chip | 4-probe | $6 \times 10^{-4}$ | Metallic | |
| $NaPt_3O_4$ | Pellet | Ac, *c* | $3 \times 10^{-2}$ | Metallic | |
| $Cd_xPt_3O_6$ | Pellet | Ac, *c* | 10 | Semiconducting | 0.05 |
| $\alpha$-$PtO_2$ | Pellet | Ac, *c* | $10^4$ | Semiconducting | 0.1 |
| $\beta$-$PtO_2$[f] | Pellet | Not given | $10^6$ | Semiconducting | 0.2 |

[a] All values at room temperature (except for $CaPd_3O_4$). [b] From ref 1a. [c] See L. J. van der Pauw, *Philips Res. Rep.*, **13**, 1 (1958). [d] From R. C. Wnuk, T. R. Touw, and B. Post, *IBM J. Res. Develop.*, **8**, 185 (1964); at 77°K. [e] From ref 16. [f] From R. D. Shannon, *Solid State Commun.*, **6**, 139 (1968); **7**, 257 (1969).

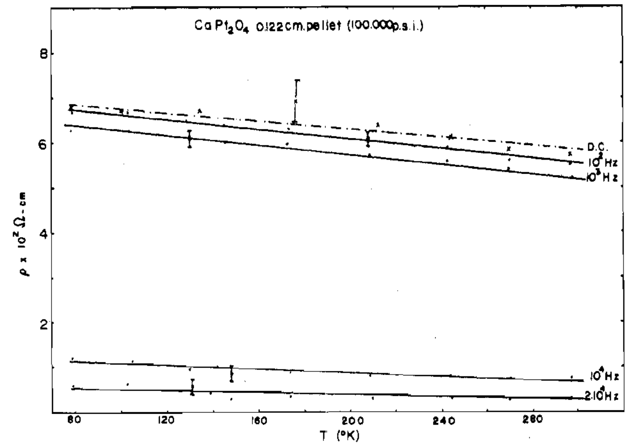

**Figure 9.** Plot of specific resisitivity *vs.* temperature for $CaPt_2O_4$ at several frequencies.

pose one has to be sure where, on the kinetic energy scale, the zero of the binding energy scale should be placed. It is obviously impossible to use the same calibration technique as the one used for the core level binding energies[11a] as the spectrum would be a superposition of the valence band of gold and the sample. Therefore the binding energies are referred to those of the Pt 4f levels of the sample, which had been calibrated previously as described elsewhere.[11a] The binding energy in the uv spectrum is referred to the Fermi energy of gold, obtained from an ion-sputtered (etched) sample of gold foil.

All spectra are dominated by the Pt 5d levels. In the sodium and calcium bronze X-ray spectra the Fermi energy falls in the middle of a steep decrease in intensity. For $Cd_xPt_3O_6$ and $\alpha$-$PtO_2$ the Fermi level energy is shifted to slightly lower kinetic energies. The general shapes of the X-ray spectra of $NaPt_3O_4$ and $CaPt_2O_4$ are rather similar, suggesting a related energy band structure. The valence band of $Cd_xPt_3O_6$ shows few features (the high binding energy peak at ~11 eV arises from the Cd 4d electrons). The uv spectrum of sodium platinum bronze, which has not been corrected for secondary electrons, has features quite different from those of the X-ray spectrum. However a correspondence is observed between shoulder and peak positions in these spectra. For metallic and semiconducting samples such differences in intensity are not uncommon.[11b,32] The uv spectrum shows a definite intensity (*i.e.*, electron density of the sample) at the Fermi level, in agreement with the X-ray spectrum.

**Discussion.** The picture that emerges from these physical properties of the bronzes agrees well with that which one would be inclined to draw on basis of knowledge of the bronze structure (Figure 2). The bronzes are metallic oxides (except for the special cases discussed below). Contrary to their tungsten namesakes the platinum bronzes are probably class I metallic oxides in Goodenough's classification.[33] In a class I metallic oxide there is a strong interaction between the d electrons on neighboring cations because of a small cation-cation separation, while in class II metallic oxides such strong interaction is brought about by a large cation-anion-cation interaction (*e.g.*, W-O-W in the tungsten bronzes). The Pt-Pt distance in the bronzes varies from 2.79 to 2.84 Å, which can be compared with a Pt-Pt separation of 2.78 Å in the pure metal. If indeed the Pt chains provide the major path for the transport of electrons, then it is very tempting to compare the conductivities of $CaPt_2O_4$ on the one hand and $NaPt_3O_4$ and $Cd_{0.3}Pt_3O_4$ on the other. Pt chains run in three dimensions with three Pt atoms per formula unit in the sodium and cadmium bronzes but such chains are present in only two dimensions with two Pt atoms per formula unit in the calcium bronze. Although our results do suggest that $CaPt_2O_4$ is a poorer conductor than $Cd_{0.3}Pt_3O_4$ or $NaPt_3O_4$, the fact that no single-crystal data are available for the calcium and cadmium bronzes makes such a comparison dangerous, if not impossible. A similar comparison, which will have to await single-crystal data, could be made with the one-dimensional Pt-chain compounds such as $K_2[Pt(CN)_4]Br_{0.3}\cdot xH_2O$.[34] Here however a proper comparison is possible only with ideal crystals that do not have stacking faults disrupting the one-dimensional chains. In all such comparisons one should bear in mind differences in the band structures of these materials. As discussed below the band structures of $CaPt_2O_4$ and the three-dimensional bronzes are probably very similar.

Note that the weak metal-metal interaction between the square-planar platinum atoms in $Cd_xPt_3O_6$ (Pt-Pt = 3.165 Å) is apparently not enough to give rise to metallic conductivity. Instead $Cd_xPt_3O_6$ is a low band gap semiconductor.

We now turn again to the puzzling question of the occurrence of $CaPt_2O_4$ instead of $CaPt_3O_4$. A more direct, be it tentative, explanation than the one given above can be found if we consider a qualitative one-electron energy-band scheme for the bronzes. The construction of such schemes has been described in detail by Goodenough.[35] Figure 12 shows such a diagram for the bronzes.

The energy levels of the cation (Pt, Pd) are shown on the left-hand side as perturbed by a square-planar crystal field.

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(32) N. V. Smith, *Crit. Rev. Solid State Sci.*, 3, 45 (1971); W. C. Price, A. W. Potts, and D. G. Streets in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam 1972, p 187 ff.

(33) J. B. Goodenough, *Progr. Solid State Chem.*, 5, 151 (1971).

(34) See, for example, T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1, 99 (1972).

(35) J. B. Goodenough, *Progr. Solid State Chem.*, 5, 223 (1971).

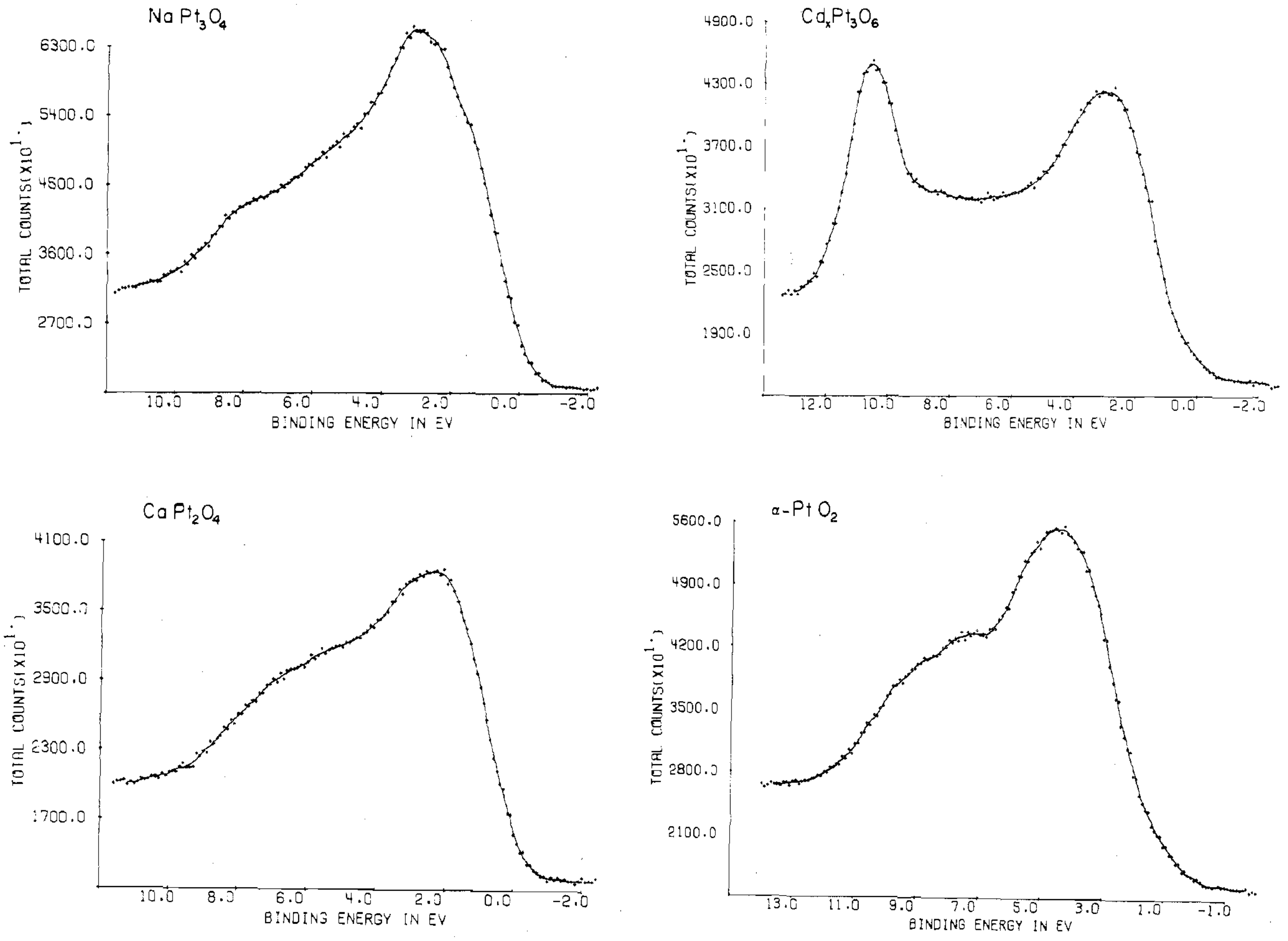

**Figure 10.** X-Ray photoelectron spectra of the valence band regions for some bronzes and other platinum oxides.

The oxygen orbitals, which split into two kinds, are shown on the right-hand side. The sp$^2$ hybridized orbitals will interact with platinum, while the remaining p orbital will be directed toward and is $\sigma$ bonding with the counterion (*e.g.*, Ni). The highest occupied band is mainly $\sigma$ with respect to Pt-Pt bonding and will be partially filled when the counterion is monovalent or when less than a stoichiometric amount of a divalent counterion is present. Such is the case in all Pt bronzes except $CdPt_3O_4$ where elemental analysis suggests the presence of one Cd per formula unit. The holes in the highest occupied band, the higher half of which is antibonding in character, strengthen the bonding along the Pt chains. In the platinum bronzes this bonding is done by 5d electrons while in the palladium bronzes the 4d electrons are used. In $CaPd_3O_4$ the highest occupied band is completely filled, resulting in a nonbonding interaction. Because the 4d electrons have a smaller radial distribution than the 5d electrons, such nonbonding interaction will not break up the structure. In calcium platinum bronze a filled antibonding band seems to give rise to too high a repulsive force between the Pt ions to permit the formation of $CaPt_3O_4$. $CaPt_2O_4$ has only a half-filled band and no electrons in the antibonding half of this band. The existence of $CdPt_3O_4$ proves that the foregoing argument cannot be the only reason influencing nonformation of the bronzes. Possibly a combination of the thermodynamic argument given before with the electronic argument given here should be used.

It is obvious from Figure 12 that if the highest occupied band is completely filled, the compound has to be semiconducting. This is indeed true for $CaPd_3O_4$.[36] Unfortunately $CdPt_3O_4$ could be prepared in only very low yields, thus making a study of its electrical properties, using polycrystalline material, impossible. Also shown in the diagram are the estimated energy levels of the counterions. Except for possibly $Ni^{2+}$ and similar ions, these ions will not play a major role in any electronic conduction. But the band scheme does illustrate two opposite forces that can influence the counterion content of the bronzes. Addition of counterions to an empty bronze will stabilize the $p_\pi$ band, which is mainly oxygen in character and is nonbonding toward platinum. However at the same time the highest occupied ($d_{z^2}$) band is filled up, a process that costs energy because of the antibonding character of the upper half of this band. The low accuracy inherent in measurements on powders precludes a meaningful comparison between, for example, $NaPt_3O_4$ and $Na_xPt_3O_4$ which differ greatly in their impurity content. Although the energy diagram does not apply strictly to the defect $NaAu_2O_3$, it seems likely that this compound is metallic. $Ag_3PO_4$ and $Ag_3AsO_4$ are probably semiconducting because of their filled d bands ($d^{10}$) and relatively large Ag-Ag separations of 3.01 and 3.06 Å, respectively.[37] ($AgBO_2$ delafossite phases with Ag-Ag separations as low as 2.87 Å all show semiconducting behavior.[38] In all these compounds silver has the $d^{10}$ configuration as well.)

The magnetic susceptibility data for the bronzes are con-

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(36) R. C. Wnuk, T. R. Touw, and B. Post, *IBM J. Res. Develop*, 8, 185 (1964).

(37) R. Blackstone, Thesis, Leyden, 1969.

(38) D. B. Rogers, R. D. Shannon, C. T. Prewitt, and J. L. Gilsson, *Inorg. Chem.*, 10, 723 (1971).

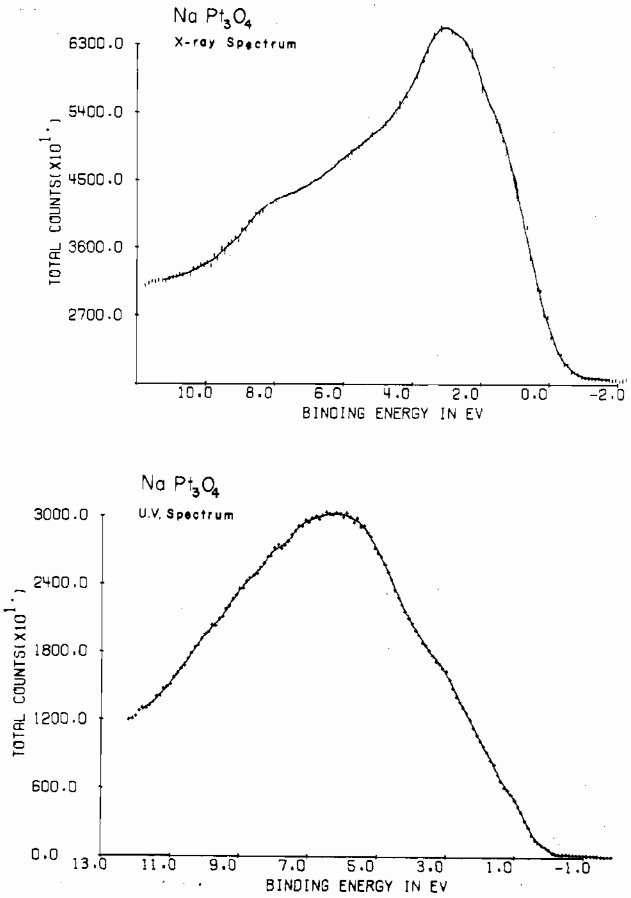

**Figure 11.** X-Ray and uv photoelectron spectra of $NaPt_3O_4$.

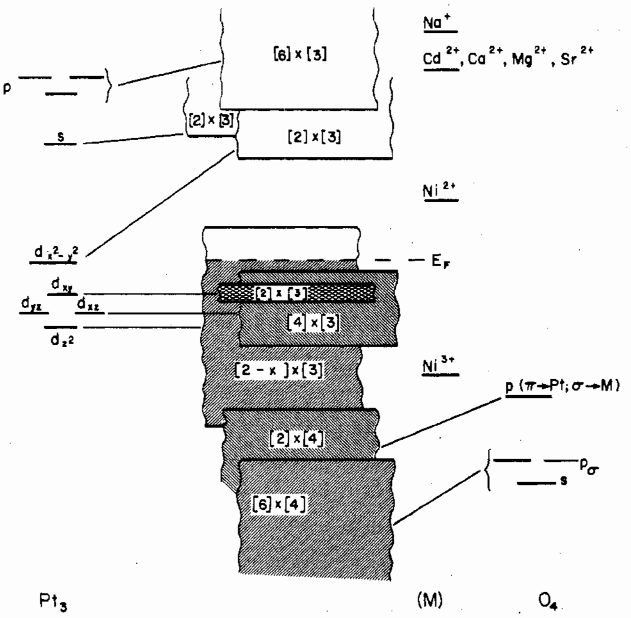

**Figure 12.** Qualitative one-electron energy-band diagram for the platinum metal bronzes.

**Table VII.** X-Ray Diffraction Powder Data for "$Pt_5O_6$"

| $d_{obsd}$,[a] Å | hkl[b] | $I_{obsd}$ | $d_{obsd}$, Å | hkl | $I_{obsd}$ |
|---|---|---|---|---|---|
| 5.491 | 002 | 7 | 2.366 | 121 | 2 |
| 5.197 | 100 | 2 | 2.245 | $\bar{2}12$ | 34 |
| 4.877 | $\bar{1}01$ | 20 | 2.218 | $\bar{2}03$ | 6 |
| 3.948 | $\bar{1}02$ | 2 | 2.057 | $\bar{2}13$ | 7 |
| 3.644 | 102 | 4 | 1.986 | $\bar{2}04$ | 1 |
| 3.105 | $\bar{1}03$ | 4 | 1.921 | 213 | 1 |
| 2.793 | 020 | 14 | 1.896 | $\bar{2}20$ | 5 |
| 2.745 | 004 | 8 | 1.872 | $\bar{2}14$ | 1 |
| 2.702 | $\bar{1}13$ | 66 | 1.834 | 006 | 4 |
| 2.645 | 021 | 33 | 1.811 | 031 | 1 |
| 2.606 | 200 | 18 | 1.720 | 025 | 3 |
| 2.562 | 113 | 5 | 1.652 | $\bar{3}10$ | 7 |
| 2.499 | 201 | 4 | 1.625 | $\bar{3}12$ | 2 |
| 2.470 | 022 | 3 | 1.611 | 116 | 2 |
| 2.436 | $\bar{1}20$ | 8 | 1.573 | 007 | 12 |

[a] Cu K$\bar{\alpha}$ radiation was used. The *d* values are calibrated against those of TlCl. [b] Indexed on the basis of the monoclinic cell mentioned in the Appendix.

sistent with their metallic character, as the conduction electrons will give rise to a Pauli temperature-independent paramagnetism.

A last point that should be noted is the apparent capability of the bronzes to incorporate any ion that will fit, as evidenced by the high impurity levels in the sodium bronzes. Since the bronzes have a cage-like structure not unlike that of certain zeolites, this is not entirely unexpected. It is very likely that most of the impurity cations are located in the channels where the counterion is situated. This high impurity level is further illustrated by the low ratio of the resistivity at room temperature to that at liquid helium temperature for the single-crystal bronze.[1a]

In summary, although the existence of these expensive oxides might be a nuisance to the high-temperature chemist, their unusual structures, interesting physical properties, and catalytic activity make them a fascinating new class of compounds. It is hoped that future single-crystal work will be able to add to the results of the present study.[38a]

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## Appendix

Muller and Roy reported the existence of an unidentified phase that is formed together with $Pt_3O_4$.[3] The X-ray diffraction pattern of the purified product of reaction VI (Table I) checks well with the peaks reported by Muller and Roy for their unidentified phase. Elemental analyses showed the material (that was free of Pt metal) to contain Pt and O in the ratio of 5:6. No other element was found to be present (the limit of detection was 0.5%). The powder pattern of the "$Pt_5O_6$" phase is listed in Table VII. It can be indexed on the basis of a small monoclinic cell ($a = 5.24$; $b = 5.51$, $c = 11.04$ Å; $\beta = 94° 53'$) or a slightly larger orthorhombic cell[39] ($a = 11.11$, $b = 5.66$, $c = 10.07$ Å). In view of the low reliability indices[40] for both cells (2.4 and 2.3, respectively) it is unlikely that these are the simplest cells possible.

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(38a) Note Added in Proof. Recently B. Bergher and R. Kohlhaas [*Z. Anorg. Allg. Chem.*, 401, 9 (1973)] reported the preparation and lattice parameters of several platinum-metal bronzes. Because of the dearth of experimental details given in their paper we are unable to comment on the discrepabcues between their work and ours.

(39) The indexing program of R. B. Roof, Jr., was used: Report LA-3920, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1968. Computations were carried out on a CDC 6400 computer.

From the cell dimensions, density (>10.6 g/cm$^3$), and chemical stability (stable toward attack by aqua regia) it is possible that this phase is related to the bronzes but clearly single crystals will have to be obtained to elucidate such a relationship.

**Registry No.** $CdCO_3$, 513-78-0; $(NH_4)_2PtCl_6$, 16919-58-7; $Na_2CO_3$, 497-19-8; Pt, 7440-06-4; $NaNO_3$, 7631-99-4; $H_2PtCl_6$, 16941-12-1; $CaCO_3$, 471-34-1; $BaO_2$, 1304-29-6; $Cd_xPt_3O_4$, 39394-68-8; $CdPt_3O_6$, 12590-34-0; $NaPt_3O_4$, 50864-26-1; $Na_xPt_3O_4$, 50958-14-0; α-$PtO_2$, 1314-15-4; $CaPt_2O_4$, 39394-82-6; $Pt_3O_4$, 12137-40-5; $Pt_5O_6$, 51021-61-5; $CoPtO_2$, 12516-23-3; $Ni_{0.25}Pt_3O_4$, 37295-01-5; $Ag_3PO_4$, 7784-09-0; $Ag_3AsO_4$, 13510-44-6.

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(40) $M_{20}$, the reliability index, is defined by P. M. deWolff, *J. Appl. Crystallogr.*, 1, 108 (1968); 5, 243 (1972).

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# Structures of Metallocarboranes. I. Crystal and Molecular Structure of 2,6-Di-η-cyclopentadienyloctahydro-1,10-dicarba-2,6-dicobalta-*closo*-decaborane at −150°, a Bimetallocarborane with a Metal–Metal Bond

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The crystal and molecular structure of 2,6-di-η-cyclopentadienyloctahydro-1,10-dicarba-2,6-dicobalta-*closo*-decaborane, 2,6-$(\eta\text{-}C_5H_5)_2$-2,6-$Co_2$-1,10-$C_2B_6H_8$, has been determined at −150° by single-crystal X-ray diffraction methods. The molecule crystallizes as green slabs in the monoclinic space group $C2/c$ with eight molecules per unit cell. At 23° $a = 28.47$ (2) Å, $b = 8.46$ (1) Å, $c = 15.28$ (1) Å, and $\beta = 129.43$ (3)° ($\rho_{\text{calcd}} = 1.61$ g/cm$^3$, $\rho_{\text{obsd}} = 1.60$ (1) g/cm$^3$). At −150° $a = 28.101$ (5) Å, $b = 8.351$ (2) Å, $c = 15.154$ (5) Å, and $\beta = 129.28$ (2)° ($\rho_{\text{calcd}} = 1.66$ g/cm$^3$). The structure was solved by direct methods and refined with 1372 reflections greater than $3\sigma(I)$ collected to $2\theta = 45°$ (Mo Kα radiation) on a Syntex $P\bar{1}$ diffractometer. The final discrepancy indices are $R = 0.034$ and $R_w = 0.043$. The polyhedral framework is a distorted bicapped square antiprism with carbons at the caps and one cobalt in each tropical plane. The cobalt atoms are joined by a 2.489 (1) Å bond, the first confirmed metal–metal bond in a bimetallocarborane.

## Introduction

The crystal structures of bimetallocarboranes had been determined prior to this work in only two cases.[1,2] In both cases the complexes contained the same polyhedral framework, $\{3,6\text{-}Co_2\text{-}1,2\text{-}C_2B_8H_{10}\}$, and they were both prepared by the same method, base degradation of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ followed by complexation of another metal. In these complexes the metal atoms are nonadjacent.

Other bimetallocarboranes are known,[3-8] and prior to preliminary disclosure of the results of this work,[9] they were in all cases assigned probable structures in accord with the structural precedents, *i.e.*, nonadjacent metal atoms.[10] However, most of the bimetallics reported since 1970 have been prepared by polyhedral expansion,[7] an entirely different route from that used to prepare the molecules whose structures were determined.[1,2]

Since the known structures were not necessarily good models for the products of polyhedral expansion, the structural investigation of $(\eta\text{-}C_5H_5)_2Co_2C_2B_6H_8$, a polyhedral expansion product,[3] was undertaken. The results described herein provide direct structural information on the stereochemical course of this reaction.

## Experimental Section

Very dark green crystals of 2,6-$(\eta\text{-}C_5H_5)_2$-2,6-$Co_2$-1,10-$C_2B_6H_8$,[12] prepared by Dunks,[3] were used without modification. Despite 2 years of atmospheric storage, no evidence of decomposition was observed.

Precession and Weissenberg photographs were taken of a plate-shaped fragment cut from a long slab. The systematic absence of reflections $hkl$ for $h + k \neq 2n$ and $h0l$ for $h \neq 2n$, $l \neq 2n$ indicated the space group to be either $Cc$ or $C2/c$. The space group was assigned as $C2/c$ based on the successful solution and refinement described herein.

Unit cell parameters were determined by least-squares refinement of 13 reflections which were accurately centered on a Syntex $P\bar{1}$ four-circle diffractometer with Mo Kα radiation and Syntex software. At 23° the lattice parameters are $a = 28.47$ (2), $b = 8.46$ (1), $c = 15.28$ (1) Å, and $\beta = 129.43$ (3)°; at −150° they are $a = 28.101$ (5), $b = 8.351$ (2), $c = 15.154$ (5) Å, and $\beta = 129.28$ (2)°. The calculated densities at 23° and −150° ($Z = 8$) are 1.61 and 1.66 g/cm$^3$, respectively, while the density determined by flotation in carbon tetrachloride–hexane at 23° is 1.60 (1) g/cm$^3$.

The structure was first solved with a set of data collected at 23° (1297 reflections with $F_o > 3\sigma(F_o)$, $2\theta \leq 50°$). However, check reflections for this set indicated significant decomposition in the X-ray beam, losing from 10 to 90% of their original intensity in 114 hr of exposure. The final structure determined from this set of data had an $R$ factor and estimated standard deviations larger than acceptable, so final refinements were based on a set of data collected at −150°.

For the low-temperature data collection a fragment of approximately rectangular dimensions 0.13 × 0.22 × 0.26 mm was cut from

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(9) (a) M. F. Hawthorne and G. B. Dunks, *Science*, 178, 462 (1972); (b) M. F. Hawthorne, *Pure Appl. Chem.*, 33, 475 (1973).

(10) Most of the bimetallic species reported since preliminary disclosure of this work have proposed structures containing metal–metal bonds[6-8] and in one other case this has now been confirmed.[11]

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(12) The other enantiomer of this compound, 2,9-$(\eta\text{-}C_5H_5)_2$-2,9-$Co_2$-1,10-$C_2B_6H_8$, was of course present in equal amount.