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Platinum Bronzes. II.[1] Crystal Structures of CaPt$_2$O$_4$ and Cd$_{0.3}$Pt$_3$O$_4$

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The crystal structures of CaPt$_2$O$_4$ and Cd$_{0.3}$Pt$_3$O$_4$ have been determined from X-ray and neutron diffraction powder data. Refinement of both X-ray and neutron intensity data led to final weighted and unweighted agreement indices of 24.6 and 16.0% for CaPt$_2$O$_4$ and 6.8 and 9.8% for the simpler Cd$_{0.3}$Pt$_3$O$_4$. CaPt$_2$O$_4$ has a structure that is the two-dimensional analog of the general platinum bronze structure. It crystallizes in space group $D_{4h}{}^9$-$P4_2/mmc$ of the tetragonal system with two formula units in a cell of dimensions $a = 5.7786$ (5) Å and $c = 5.5989$ (7) Å. The structure appears to be a unique one involving nonintersecting Pt chains in the x and y directions. Pt chain compounds in one and three dimensions are known and CaPt$_2$O$_4$ forms the missing two-dimensional link. Cd$_{0.3}$Pt$_3$O$_4$ possesses the NiPt$_3$O$_4$ structure involving Pt chains in the x, y, and z directions. It crystallizes in space group $O_h{}^3$-$Pm3n$ of the cubic system with two formula units in a cell with a cell edge of 5.6423 (4) Å. The unusual formal oxidation states of Pt in both compounds are explained by extensive metallic bonding between the Pt atoms.

Introduction

Interest in the oxides of platinum arises first of all from their very existence. Platinum metal is used extensively as an inert material in high-temperature chemistry. Knowledge of the conditions under which the metal will react chemically is therefore of considerable importance. A further incentive for study of these oxides is the catalytic activity of some ill-defined platinum oxides, as exemplified by Adams' catalyst.[3]

Platinum bronzes are ternary oxides of platinum with the general formula M$_x$Pt$_3$O$_4$, where M is generally a group I or II cation and x ranges from zero to one. Palladium also forms this type of oxide. With Pd as the central metal, the Na, Ca, Cd, and Sr bronzes have been synthesized, while with Pt, the Na, Mg, and Ni bronzes are known.[1] While attempting to prepare CaPt$_3$O$_4$ we obtained the phases CaPt$_2$O$_4$ and Ca$_4$PtO$_6$. Both these materials were first prepared by Post[4] and later by McDaniel.[5] Czaya accidentally prepared single crystals of Ca$_4$PtO$_6$ during syntheses of calcium silicates in a platinum crucible using a CaCl$_2$ flux.[6] All of our attempts to prepare single crystals of CaPt$_2$O$_4$ at atmospheric pressure have been fruitless. CdPt$_3$O$_4$ has not been reported before. We have prepared both Cd$_{0.3}$Pt$_3$O$_4$ and Cd$_1$Pt$_3$O$_4$, thereby proving for the first time that x in M$_x$Pt$_3$O$_4$ is truly a variable, as was first suggested by Waser and McClanahan for Na$_x$Pt$_3$O$_4$.[7] No single crystals were obtained.

The unit cell of CaPt$_2$O$_4$ suggested that its structure might be related to that of Ni$_x$Pt$_3$O$_4$,[1] *i.e.*, the general platinum bronze structure. From initial inspection of the powder diffraction pattern it was clear that only a few variables would have to be determined in order to solve the structure. The pattern furthermore showed no resemblance to that of any of the known AB$_2$O$_4$ structures. Therefore, a combined X-ray and neutron powder diffraction study was undertaken.

Only Cd$_{0.3}$Pt$_3$O$_4$ could be prepared in sufficient quantity to carry out a neutron diffraction study. The X-ray powder diffraction pattern of Cd$_{0.3}$Pt$_3$O$_4$ shows that it has the general platinum bronze structure. Since Cd is a better X-ray scatterer than Ni or Na, we hoped to find out in the present instance whether the counterions (Cd^{2+}) are ordered or randomly distributed over the available lattice sites. Furthermore, because the earlier X-ray diffraction study on Ni$_x$Pt$_3$O$_4$ failed to distinguish between a centric and noncentric structure, an X-ray and neutron study was carried out on Cd$_{0.3}$Pt$_3$O$_4$ in order to try to resolve these problems.

Experimental Section

Both CaPt$_2$O$_4$ and Cd$_{0.3}$Pt$_3$O$_4$ were prepared by the reaction of (NH$_4$)$_2$PtCl$_6$ with the corresponding carbonate under an atmosphere of O$_2$.[8]

X-Ray powder diffraction data for CaPt$_2$O$_4$ were collected in the continuous scan mode on a Picker diffractometer. Monochromatic Co K$\bar{\alpha}$ radiation was obtained from the (200) plane of a LiF crystal. X-Ray powder data for Cd$_{0.3}$Pt$_3$O$_4$ were collected in the step-scan mode on a Norelco diffractometer. Monochromatic Cu K$\bar{\alpha}$ radiation was obtained from the (002) plane of a graphite crystal. In both instances the samples were approximately 2 mm thick and were in the flat-plate geometry. Accordingly, no correction for absorption is necessary.[9]

The neutron diffraction data were obtained with the Argonne computer aided diffraction equipment[10] at the CP-5 reactor. The data for CaPt$_2$O$_4$ were collected on the heavy-duty powder unit with $\lambda = 1.20$ Å obtained from the (111) plane of a germanium monochromator. Two θ step scans (0.2° step) were timed with a fission monitor (approximately 15 min/step). Data for Cd$_{0.3}$Pt$_3$O$_4$ were obtained from the smaller unit, *i.e.*, a Picker X-ray unit modified for neutron diffraction. Its monochromatic beam (1.050 Å) is obtained in transmission from the (110) planes of a Be single crystal. Step scans were also obtained in 0.2° steps for a time of approximately 15 min per point. Samples were loaded in cylindrical vanadium cans (5 mil wall thickness) with a diameter of $^3/_8$ in. for CaPt$_2$O$_4$ and 0.25 in. for Cd$_{0.3}$Pt$_3$O$_4$. The correction for absorption of the data from CaPt$_2$O$_4$ proved to be negligible; that for Cd$_{0.3}$Pt$_3$O$_4$ was not since the linear absorption coefficient is 1.25 cm^{-1}.[11] The usual correction for cylindrical geometry was therefore made, based on the measured packing density of 0.25.

The powder spectra for CaPt$_2$O$_4$ were fully indexed on the basis of a tetragonal unit cell of dimensions $a = 5.7786$ (5) and $c = 5.5989$ (7) Å based on the least-squares refinement of the X-ray line positions calibrated against TlCl ($a = 3.8421$ Å).[12] The theoretical density for two formula units in the cell is 8.8 g/cm^3. From pycnometric measurements on the extremely finely powdered material a lower limit for the observed density is 7 g/cm^3.

The powder spectra for Cd$_{0.3}$Pt$_3$O$_4$ were indexed on the basis of

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[1] For the first paper in this series, see D. Cahen, J. A. Ibers, and R. D. Shannon, *Inorg. Chem.*, 11, 2311 (1972).

[2] (a) Northwestern University; (b) Argonne National Laboratory.

[3] See, for example, Paul N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York and London, 1967, p 312.

[4] B. Post, private communication; Powder Data File, Card No. 15-520, Joint Committee on Powder Diffraction Standards, Swarthmore, Pa.

[5] C. L. McDaniel, *J. Amer. Ceram. Soc.*, 55, 426 (1972).

[6] R. Czaya, *Z. Anorg. Allg. Chem.*, 375, 61 (1970).

[7] (a) J. Waser and E. D. McClanahan, Jr., *J. Chem. Phys.*, 19, 413 (1951); (b) *ibid.*, 20, 199 (1952).

[8] D. Cahen, J. A. Ibers, and J. B. Wagner, Jr., submitted to *Inorg. Chem.*

[9] (a) H. Lipson and H. Steeple, "Interpretation of X-Ray Powder Diffraction Patterns," Macmillan, London, 1970, p 94 ff; (b) B. D. Cullity, "Elements of X-Ray Diffraction," Addison-Wesley, Reading, Mass., 1967, p 188 ff.

[10] M. H. Mueller, *Advan. X-Ray Anal.*, 15, 70 (1972).

[11] K. Weber, *Acta Crystallogr.*, 23, 720 (1967).

[12] Powder Data File, Card No. 6-0486, Joint Committee on Powder Diffraction Standards, Swarthmore, Pa.

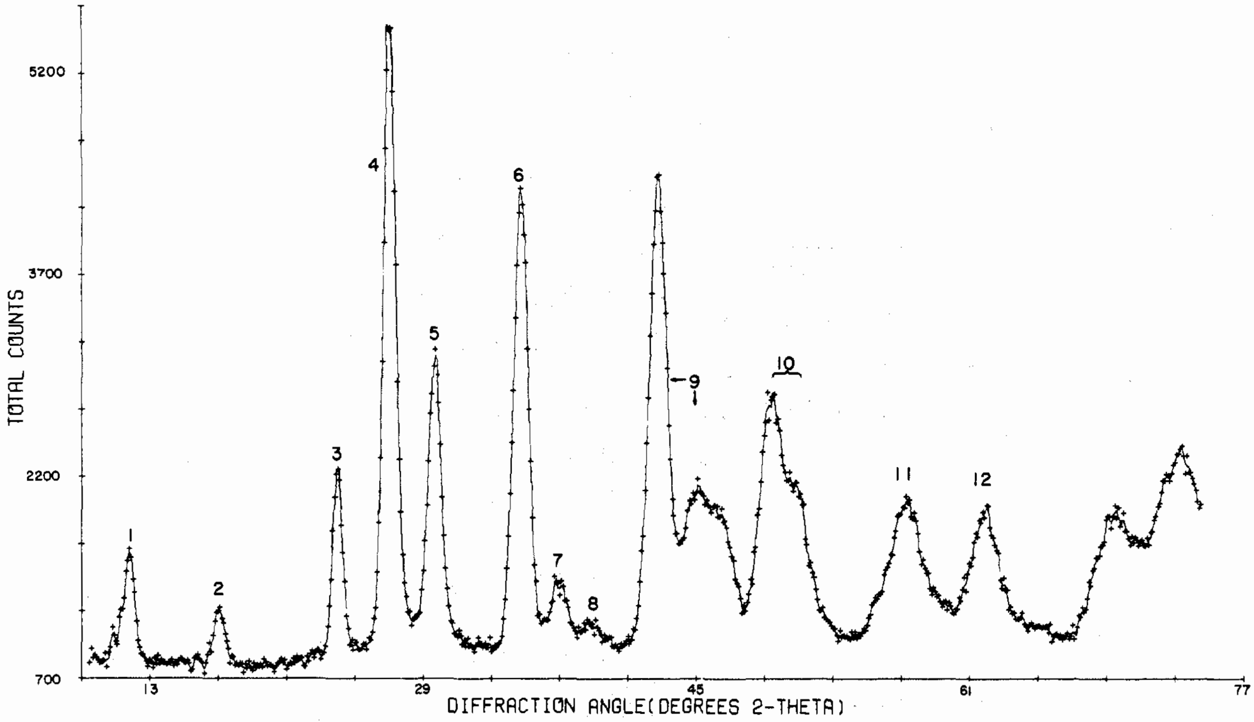

Figure 1. Neutron diffraction data for $CaPt_2O_4$. A five-point smoothed line is drawn through the experimental points. The peak numbers refer to those in Table I.

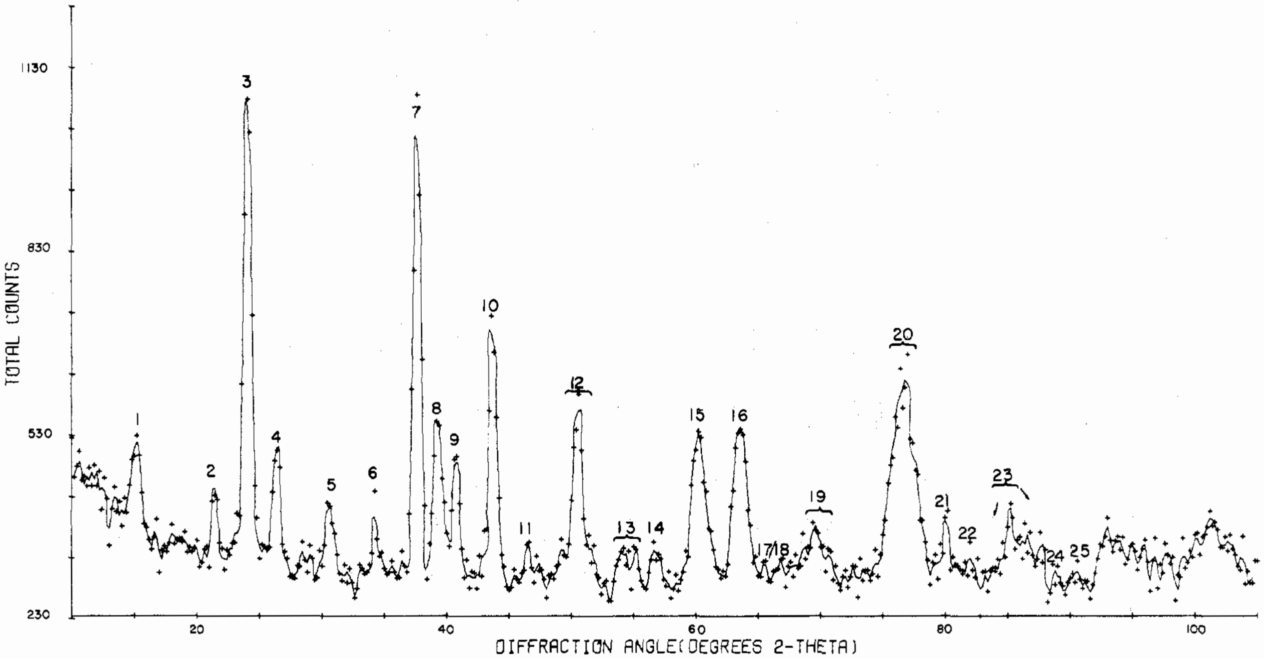

Figure 2. Neutron diffraction data for $Cd_{0.3}Pt_3O_4$. A five-point smoothed curve is drawn through the experimental points. The peak numbers refer to those in Table III.

a cubic unit cell with edge 5.6423 (4) Å, again obtained from a least-squares analysis of the calibrated X-ray line positions. This cell edge may be compared with $a = 5.688$ Å for $Cd_1Pt_3O_4$. The theoretical density of 12.7 g/cm^3 for four formula units in the cell may be compared with a lower limit to the experimental density of 8 g/cm^3.

Figures 1 and 2 show the experimental neutron diffraction data for the two compounds. The X-ray data are not shown but are of comparable quality.

Intensities were obtained from the graphed spectra, using a Keuffel and Esser Model 620015 compensating polar planimeter, and standard deviations in these intensities were estimated taking into account the counting statistics and the base levels of the peaks.

Tables I and II give the fully indexed neutron and X-ray powder patterns of $CaPt_2O_4$. The numbers of the observed peaks in Table I refer to those in Figure 1. The 2θ angle is given in degrees. Thus, we confirm the tetragonal unit cell proposed by Post.[3] Systematic absences were observed for $l = 2n + 1$ in the hhl reflections. The possible space groups are then $P4_2/mmc$, $P\bar{4}2c$, or $P4_2mc$. Because of the overlap of intensity data we could not distinguish between these possibilities and therefore the space group with highest symmetry, $D_{4h}{}^9$-$P4_2/mmc$, was chosen.

The powder patterns of $Cd_{0.3}Pt_3O_4$ for neutrons and X-rays are given in Tables III and IV. The observed intensities in Table III have been corrected for absorption. The pattern fits that of the general Pt bronze structure. The space group is either $O_h{}^3$-$Pm3n$ or $T_d{}^4n$-$P\bar{4}3n$ based on the absence of hhl for l odd.

Structure Refinement

Refinement of the structures was effected through the method of least squares[13] in which the function minimized is $\Sigma w(I_o - I_c)^2$, where

TABLE I

$CaPt_2O_4$ Neutron Diffraction Data

$\lambda = 1.20$ Å

# (Obs)	2θ	hkℓ	d_c	$I_c \times 10^{-2}$	$\Sigma I_c \times 10^{-2}$	$I_o \times 10^{-2}$	$\sigma(I_o) \times 10^{-2}$
1	11.9	100	5.779	106	106	91	1
2	16.9	110	4.086	11	45	41	2
	17.2	101	4.021	34			
3	24.0	200	2.889	154	154	107	2
4	26.8	210	2.584	31	406	447	6
	27.0	201	2.568	263			
	27.6	102	2.519	112			
5	29.6	211	2.346	246	253	244	3
	30.1	112	2.309	7			
6	34.2	220	2.043	13	332	374	6
	34.7	202	2.011	319			
7	36.3	300	1.926	50	152	78	8
	36.8	212	1.899	103			
8	38.3	310	1.827	12	30	36	6
	38.5	301	1.821	18			
9	42.6	222	1.650	406	749	819	9
	44.0	320	1.603	93			
	44.4	302	1.587	0			
	45.0	203	1.558	92			
	45.8	321	1.541	66			
	46.2	312	1.530	7			
	46.7	213	1.513	86			
10	49.1	400	1.445	204	360	500	7
	50.7	410	1.402	11			
	50.8	004	1.400	106			
	51.1	322	1.391	4			
	52.3	330	1.362	1.4			
	52.4	104	1.360	10			
	52.4	411	1.360	11			
	53.2	303	1.340	11			
	53.9	114	1.324	0.6			
11	54.7	313	1.306	1.4	335	281	8
	55.3	420	1.292	55			
	55.7	402	1.284	0			
	56.9	204	1.260	65			
	56.9	421	1.259	110			
	57.2	412	1.253	46			
	58.4	214	1.231	12			
	58.7	332	1.225	11			
	59.1	323	1.216	34			
12	61.5	422	1.173	153	253	236	6
	62.6	500	1.156	0			
	62.6	430	1.156	29			
	62.6	224	1.155	6			
	63.4	403	1.142	0			
	63.9	510	1.133	0.3			
	64.0	304	1.132	31			
	64.0	501	1.132	2			
	64.0	431	1.132	16			
	64.7	413	1.121	9			
	65.4	314	1.111	5			
	65.4	511	1.111	0.9			

TABLE II

$CaPt_2O_4$ X-Ray Diffraction Data

$\lambda = 1.7901$ Å

# (obs)	hkℓ	d_o	d_c	I_c	ΣI_c	I_o	$\sigma(I_o)$
1	010	5.780	5.779	250	250	113	20
	001		5.599	0			
2	110		4.086	2	112	87	10
	101	4.017	4.021	110			
3	200	2.793	2.799	75	75	93	3
4	210		2.584	59	419	428	7
	201	2.567	2.568	280			
	102	2.523	2.519	80			
5	211	2.345	2.346	172	173	152	5
	112		2.309	1			
6	220	2.042	2.043	41	41	29	4
7	202	2.010	2.010	10	10	13	5
8	300		1.926	14	72	50	7
	212	1.897	1.899	58			
9	310		1.827	2	27	20	5
	301	1.823	1.821	25			
10	103	1.776	1.776	15	15	4	2
11	222	1.651	1.650	89	89	98	3
12	320	1.604	1.603	28	28	33	8
13	302		1.587	10	10	6	4
14	203	1.568	1.568	68	68	86	10
15	321	1.541	1.541	32	32	36	7
16	312		1.530	2	2	3	2
17	213	1.514	1.513	44	44	50	4
18	400	1.445	1.445	38	38	49	3
19	410		1.402	12	57	76	7
	004	1.398	1.400	18			
	322		1.391	27			
20	330		1.362	1	27	16	4
	104	1.360	1.360	12			
	411		1.360	14			
21	402	1.286	1.284	34	34	30	4
22	421		1.259	72	92	96	2
	412		1.253	20			
23	214	1.230	1.231	15	17	6	2
	332		1.225	2			
24	323	1.217	1.216	16	16	5	3
25	422		1.173	2	2	1	4
26	500	1.156	1.156	5	32	14	7
	430		1.156	6			
	224		1.155	21			
27	403		1.142	0	0	1	0.5
28	510	1.133	1.133	1	26	13	11
	304		1.133	6			
	501		1.132	3			
	431		1.132	16			
29	520		1.073	3	78	95	24
	502		1.068	13			
	432		1.068	8			
	423	1.062	1.062	54			
30	324	1.055	1.054	21	46	57	24
	521		1.054	25			
31	512		1.050	1	1	3	6
32	205	1.044	1.044	28	28	30	2
33	215		1.028	18	36	29	5
	440	1.023	1.022	18			
34	404	1.006	1.005	37	48	63	6
	522		1.002	11			
35	414	.991	.990	15	15	9	2
36	503	.984	.983	3	19	13	2
	433	.984	.983	16			
37	442	.960	.960	28	28	29	2
38	obs(29) + obs (30)				152	125	31

TABLE III

$Cd_{0.3}Pt_3O_4$ Neutron Diffraction Data

$\lambda = 1.050$ Å

# (Obs)	2θ	hkℓ	d_c	I_c	ΣI_c	I_o	$\sigma(I_o)$
1	15.1	110	3.990	379	379	390	54
2	21.4	200	2.821	206	206	195	29
3	24.0	210	2.523	1555	1555	1562	55
4	26.4	211	2.303	40	40	385	41
5	30.5	220	1.995	276	276	284	47
6	34.2	310	1.784	153	153	167	45
7	37.6	222	1.629	1484	1484	1431	52
8	39.2	320	1.565	587	587	548	48
9	40.8	321	1.508	329	329	362	52
10	43.7	400	1.411	887	887	1002	45
11	46.5	411	1.330	86	129	73	36
	46.5	330	1.330	43			
12	49.2	420	1.262	152	968	947	42
	50.5	421	1.231	715			
	51.8	332	1.203	101			
13	54.2	422	1.152	161	161	300	48
14	56.6	510	1.106	60	181	200	38
	56.6	431	1.106	121			
15	60.2	520	1.048	255	909	890	42
	60.2	432	1.048	511			
	61.3	521	1.030	143			
16	63.5	440	.997	841	841	849	40
17	65.7	530	.968	47	94	27	14
	65.7	433	.968	47			
18	66.8	531	.954	0	0	61	32
19	67.9	600	.940	20	463	487	61
	67.9	442	.940	79			
	69.0	610	.928	199			
	70.0	611	.915	55			
	70.0	532	.915	110			
20	74.2	541	.871	76	1790	1856	59
	76.2	622	.851	1137			
	77.2	630	.841	163			
	77.2	542	.841	325			
	78.3	631	.832	89			
21	80.3	444	.814	362	362	163	70
22	82.3	710	.798	33	114	68	34
	82.3	550	.798	16			
	82.3	543	.798	65			
23	84.3	640	.782	52	619	775	78
	85.3	720	.775	139			
	85.3	641	.775	277			
	86.3	721	.768	75			
	86.3	552	.768	38			
	86.3	633	.768	38			
24	88.3	642	.754	112	112	47	28
25	90.2	730	.741	30	30	88	40

TABLE IV

$Cd_{0.3}Pt_3O_4$ X-Ray Diffraction Data

$\lambda = 1.54178$ Å

# (Obs)	hkℓ	d_o	d_c	I_c	ΣI_c	I_o	$\sigma(I_o)$
1	110	3.994	3.990	649	649	610	25
2	200	2.822	2.821	130	130	290	34
3	210	2.522	2.523	2328	2328	2395	49
4	211	2.303	2.303	624	624	565	24
5	220	1.997	1.995	28	28	32	11
6	310	1.787	1.784	121	121	127	17
7	222	1.631	1.629	430	430	470	22
8	320	1.566	1.565	444	444	430	31
9	321	1.509	1.508	267	267	265	25
10	400	1.410	1.411	223	223	232	15
11	411		1.330	39	58	56	15
	330		1.330	19			
12	420	1.262	1.262	34	34	33	11.5
13	421	1.231	1.231	331	331	331	18
14	332		1.203	51	51	35	12
15	422		1.152	9	9	9	6
16	510		1.106	19	56	46	13.5
	431		1.106	37			
17	520	1.048	1.048	88	265	266	25
	432	1.048	1.048	177			
18	521		1.030	56	56	40	12.5
19	440	.998	.997	114	114	106	16
20	610	.927	.928	64	64	68	12
21	611		.915	21	63	57	15
	532		.915	42			
22	622	.850	.851	155	155	155	19
23	630	.841	.841	62	186	186	21
	542	.841	.841	124			

I_o is the absorption-corrected intensity and where I_c is the intensity calculated for that particular reflection or group of overlapping reflections and where $w = 1/\sigma^2(I_o)$. Calculated intensities were based on the usual Lorentz-polarization factors, multiplicities, and appropriate scattering factors. For the X-ray data the atomic scattering factors for neutral Ca, Cd, Pt, and O atoms were from the calculations of Cromer and Waber.[14] Anomalous dispersion terms for Co $K\bar{\alpha}$ radiation were taken from Cooper[15] while those for Cu $K\bar{\alpha}$ radiation were taken from Cromer and Liberman.[16] The neutron scattering factors were from the tabulation by Bacon.[17] Agreement indices are defined as

$$R = (\Sigma |I_o - I_c| / \Sigma I_o) \times 100$$

and

$$R_w = ((\Sigma w(I_o - I_c)^2 / \Sigma w I_o^2)^{1/2}) \times 100$$

$CaPt_2O_4$. Post concluded that the Pt atoms occupy the 4j (x, 0, 0ↄ) positions in $P4_2/mmc$. Our crystallographic data exclude any positions which impose further systematic absences, besides the general condition hhl, $l = 2n + 1$ (see Table II). This leaves two possible unique positions for the platinum. Crystal packing and approximate bond distance calculations supported Post's initial choice. The neutron diffraction data show that the most likely positions for the oxygen atoms are in 8n (x, x, $^1/_4$ↄ). With Pt and O in these positions, the only chemically reasonable position for the Ca atom is in 2c (0, $^1/_2$, 0ↄ). With the atoms placed in these positions, only two positional parameters need to be determined, namely those of Pt and O. A model showed that the most satisfying structure was obtained if both these parameters were chosen as $^1/_4$. These were the initial parameters for the least-squares refinement. The strategy of refinement took into account the relative scattering powers of the various atoms for X-rays and neutrons (Table V). Thus, the Pt positional parameter (and later the temperature factor as well) was varied in the refinement of the X-ray data. These parameters were then held constant in the refinement of the neutron data, while the oxygen positional parameter (and later its temperature factor) was varied. Initial temperature factors were zero, and only after the positional parameters had been refined were the temperature factors added as variables. Finally an attempt was made to vary the Ca temperature factor, using both data sets separately.

Because of the highly unusual structure that resulted, a structure that contains large voids and somewhat unusual coordination of the oxygen atoms, a difference Fourier synthesis was calculated. Such a synthesis, calculated from overlapping powder diffraction data, will be impossible unless one either omits all overlapping reflections or estimates the intensities for individual reflections which overlap one another. We took the latter approach using the following calculation. If I_o contains $\mathbf{h}_1, \mathbf{h}_2, \cdots$, etc., then

$$I_o(\mathbf{h}_i) = I_c(\mathbf{h}_i) \frac{\sum_i I_o(\mathbf{h}_i)}{\sum_i I_c(\mathbf{h}_i)}$$

Here $\Sigma_i I_o(\mathbf{h}_i)$ is the observed intensity of all the overlapping reflections, and $\Sigma_i I_c(\mathbf{h}_i)$ is the intensity calculated according to the model structure. From $I_o(\mathbf{h}_i)$, $F_o(\mathbf{h}_i)$ is readily derived. The values of $F_o(\mathbf{h}_i)$ along with the calculated phase for $\mathbf{h}_i$ were used in the difference Fourier summation. Because of the smaller number of overlapping reflections this calculation was based on X-ray data. The resulting difference map is featureless as it shows no peaks above 1 e/Å^3. We also attempted to vary the Pt occupancy factor and simultaneously to insert some electron density in the position that would correspond to that of a third Pt atom as found in the general bronze structure (2e or 4g). No change in the Pt occupancy factor was observed, and the occupancy factor of an additional Pt atom refined essentially to zero.

Table V. Relative Contribution to F^2 in Neutron and X-Ray Spectra ($2\theta = 0°$)

	$CaPt_2O_4$			$Cd_{0.3}Pt_3O_4$		
	% Ca	% Pt	% O	% Cd	% Pt	% O
X-Ray	3	95	2	4	95	1
Neutron	7	53	39	1	66	33

The final agreement indices reflect the serious overlap problem encountered and are $R_w = 16.9$ and 18.3%, and $R = 24.6$ and 16.0% for the X-ray and neutron data, respectively. The final parameters are given in Table VI.

$Cd_{0.3}Pt_3O_4$. The powder patterns of $Cd_{0.3}Pt_3O_4$ clearly showed that it is isotypical with $Ni_{0.25}Pt_3O_4$.[1] A careful scan was made in order to try to detect any extra peaks that might result from a possible ordering of the Cd ions. No peaks were observed that could not be indexed on the basis of the simple Pt bronze structure.

We refined the X-ray data using the positional parameters of the centrosymmetric Ni bronze structure. Subsequently, the neutron data were refined both in space groups $Pm3n$ and in the noncentrosymmetric group $P\bar{4}3n$, the only difference being the positional parameters of the oxygen atoms [($^1/_4$, $^1/_4$, $^1/_4$ↄ) in $Pm3n$ and (x, x, xↄ) in $P\bar{4}3n$]. The value of R_w obtained for $x = 0.24$ was 13.3% and was higher for x values farther away from 0.25, while it was 11.4% for $x = 0.25$. Thus the structure seems to be centrosymmetric. (A noncentrosymmetric bronze-like structure has been reported for Ag_3PO_4 and Ag_3AsO_4.[18])

Because of the nonstoichiometry of $Cd_{0.3}Pt_3O_4$ the Cd occupancy factor was varied in the refinement of the X-ray data set. The final value (0.31 ± 0.05) agrees reasonably well with that obtained from wet chemical analysis (0.22 ± 0.02). In the refinement of the X-ray data, the oxygen temperature factor was not varied, while with the neutron data the Cd occupancy factor was held constant. The final agreement indices, R_w and R, were 11.4 and 9.8% for the neutron data and 8.7 and 6.8% for the X-ray data. The final parameters obtained from these refinements are given in Table VII.

Discussion

Figure 3 shows an overall view of the crystal structure of $CaPt_2O_4$. The result is a highly unusual arrangement and, as far as we know, a unique one. The striking features of the structure are the nonintersecting Pt chains in the x and y direction, the loose packing, and the coordination of the oxygen atoms. Many two-dimensional chain compounds are known, but all of these are better described as layer compounds [*e.g.*, TaS_2, $HgPbP_{14}$, and silicates such as $Mg_3(Si_4O_{10})(OH)_2$[19]]. The only other known material with an arrangement resembling that of $CaPt_2O_4$ is $Hg_{2.85}AsF_6$, which has Hg chains in two dimensions.[20] Pt chain compounds in one and three dimensions are known[1,21] and $CaPt_2O_4$ forms the missing two-dimensional link.

The AB_2O_4 stoichiometry is a quite common one for ternary oxides. Kugimiya and Steinfink[22] have reviewed the crystal chemistry of these oxides. They propose a scheme for grouping the AB_2O_4 oxides into several known structure types, based on a plot of a "force constant" *vs.* radius ratio. Their force constant is defined as

$$K_{ab} = X_a X_b / r_e^2$$

where $r_e^2 = (r_a + r_0)^2 + (r_b + r_0)^2 + 1.55(r_a + r_0)(r_b + r_0)$ and the radius ratio is r_a/r_b. X_a and X_b are the electronegativities of A and B. For $CaPt_2O_4$ one obtains a value of 0.91 for K_{ab} and 1.62 for r_a/r_b.[23] This places the com-

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(13) A local program, NUPOWLS, was used for the least-squares refinement of the intensity data. This program is based on an earlier version by W. C. Hamilton, as described in W. C. Hamilton and J. A. Ibers, *Acta Crystallogr.*, 16, 1209 (1963), except for the fact that a diagonal weight matrix (no correlation) was used. In addition to other local programs, the following programs were used: Zalkin's FORDAP, Busing and Levy's ORFFE, and Johnson's ORTEPII.

(14) D. T. Cromer and J. T. Waber in "International Tables for X-Ray Diffraction," Vol. IV, Kynoch Press, Birmingham, England, in press.

(15) M. J. Cooper, *Acta Crystallogr.*, 16, 1067 (1963).

(16) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(17) (a) G. E. Bacon, "Neutron Diffraction," Oxford University Press, London, 1962, pp 31 ff. (b) (Cd) = $(0.38 + i\,0.13)10^{-12}$ cm was used and Cd was treated as an anomalous scatter.

(18) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience, New York, N. Y., 1965, p 152.

(19) See, for example, H. Krebs, "Fundamentals of Inorganic Crystal Chemistry," P. H. L. Walter, translator, McGraw-Hill, London, 1968.

(20) R. J. Gillespie, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, No. INOR-1.

(21) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, 8, 35 (1969).

(22) K. Kugimiya and H. Steinfink, *Inorg. Chem.*, 7, 1762 (1968).

Table VI. Final Parameters for $CaPt_2O_4$ from Neutron and X-Ray Data

	x	y	z	Wyckoff notation	Site symmetry	B, Å^2
Ca	0	$^1/_2$	0	2c	*mmm*	3.9 (2.2)[a]
Pt	0.242 (4)	0	0	4j	*mm*	0.7 (2)
O	0.268 (7)	0.268	$^1/_4$	8n	2	0.7 (9)

[a] Errors in parentheses.

Table VII. $Cd_{0.3}Pt_3O_4$ Final Parameters from X-Ray and Neutron Data

	x	y	z	Occupancy	B, Å^2	Wyckoff notation	Site symmetry
Cd	0	0	0	0.31 (3)[a]	2.5[b]	2a	$m\bar{3}$
Pt	$^1/_4$	0	$^1/_2$	3[b]	0.6 (2)	6c	$\bar{4}2m$
O	$^1/_4$	$^1/_4$	$^1/_4$	4[b]	1.9 (1)	8e	32

[a] Errors in parentheses. [b] Not varied in refinement.

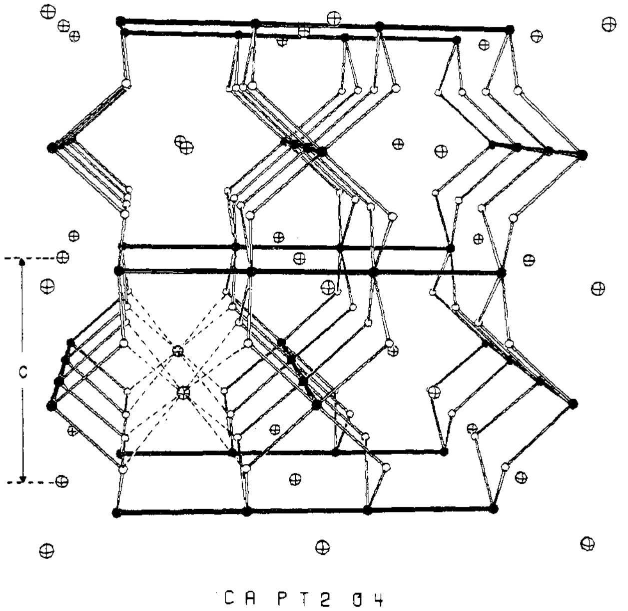

Figure 3. Crystal structure of $CaPt_2O_4$. The platinum and oxygen atoms are drawn as solid and open circles, respectively. The coordination of oxygen atoms around Ca is indicated in the lower left corner.

pound on the borderline between the $BaAl_2O_4$ and normal spinel structure in their diagram. Although this might indicate some unusual behavior for $CaPt_2O_4$, it does not explain its structure which bears no resemblance to either of the two adjacent structure types.

$CaRh_2O_4$ has been reported to possess the $CaFe_2O_4$ structure.[24] Muller-Buschbaum and von Schenck have argued that $A^{II}B^{III}{}_2O_4$ compounds will tend to attain the $CaFe_2O_4$ structure if $r_a > r_b$, a condition clearly fulfilled for $CaPt_2O_4$.[25]

It seems clear that the structure of $CaPt_2O_4$ is not readily explained if considered separately from those of other platinum bronzes. If one compares Figure 4, which shows the structure of $Cd_{0.3}Pt_3O_4$, the general bronze structure, with Figure 3, one sees a striking similarity. By removing the chains of Pt atoms in the z direction from $Cd_{0.3}Pt_3O_4$, we essentially derive the $CaPt_2O_4$ structure. The reason for the unusual behavior of Ca^{2+} is not clear as "$CaPt_3O_4$" would fit very well in the bronze stability field. One factor that might cause $CaPt_2O_4$ to behave differently is its relatively high formation temperature and its exceptional stability as compared with that of other Pt bronzes.[8]

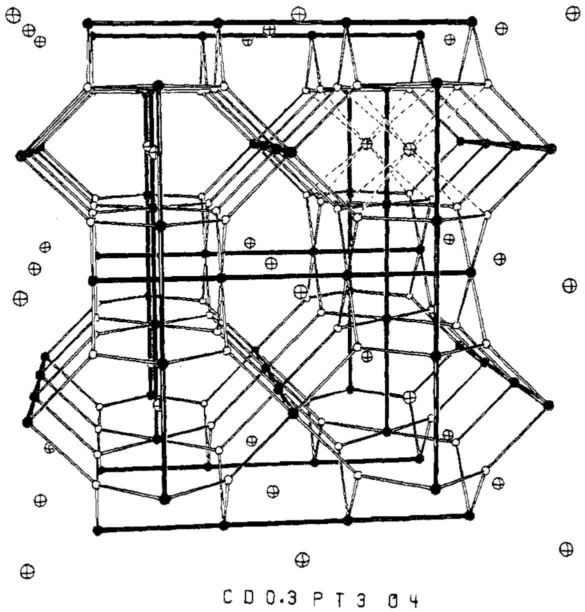

Figure 4. Crystal structure of $Cd_{0.3}Pt_3O_4$. The oxygen atoms are drawn as open circles and the platinum atoms as solid ones. The coordination of oxygen atoms around Cd is indicated in the upper right corner.

Table VIII. Selected Bond Distances (Å) and Angles (deg) in $CaPt_2O_4$

		Distances			
Pt_2-Pt_2	2.79 (5)[a]	1[b]	O-O	2.68 (8)	2
Pt_1-Pt_3	2.99 (5)	1		2.7994 (3)	2
Pt-O	2.09 (3)	4		3.09 (8)	2
Pt-Ca_1	3.17 (1)	2	Ca-O	2.481 (3)	8
Pt-Ca_2	3.21 (1)	2			
		Angles			
O-Pt-O	95 (1)	2	Pt_1-O-Pt_2	110 (3)	1
	171 (2)	2	Ca-O-Ca	173 (3)	1
	84 (2)	2	O-Ca-O	65 (2)	4
O-Pt_1-Pt_2	94 (1)	4		68.7 (1)	4
O-Pt_1-Pt_3	86 (1)	4		77 (2)	4
Pt-O-Ca	87.4 (9)	2		102 (2)	4
	88.7 (9)	2		113 (1)	4
				114 (2)	4
				180 (0)	4

[a] Errors in parentheses. [b] Number of equivalent distances (or angles).

Table IX. Interatomic Distances (Å) in $Cd_{0.3}Pt_3O_4$

Pt-O	1.9948 (2)[a]	4[b]	O-O	2.8211 (2)	6
Pt-Pt	2.8211 (2)	2	O-Cd	2.4432 (2)	8
Pt-Cd	3.1541 (2)	4			

[a] Errors in parentheses. [b] Number of equivalent distances.

Bonding in $CaPt_2O_4$ and $Cd_{0.3}Pt_3O_4$. Tables VIII and IX summarize the bond distances and angles for $CaPt_2O_4$ and $Cd_{0.3}Pt_3O_4$. No unusual distances or coordination are seen in $Cd_{0.3}Pt_3O_4$, except that here, contrary to the Ni ions in $Ni_{0.25}Pt_3O_4$, the Cd ions do fit very well in the channels formed by the oxygen atoms. The sum of the Cd^{2+} (VIII) and O^{2-} ionic radii is 2.47 Å, which compares well with the

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(23) All ionic radii in this discussion were taken or adapted from the compilations by R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B,* **25**, 925 (1969); **26**, 1046 (1970). $r\,[Ca^{2+}$ (VIII)] = 1.12 Å; $r\,[Cd^{2+}$ (VIII)] = 1.07 Å; $r\,[O^{2-}]$ = 1.40 Å; $r\,[Pt^{2+}$ (IV)] = 0.60 Å; $r\,[Pt^{3+}$ (IV)] = 0.69 Å. The Roman numerals indicate the coordination number of the ion.

(24) J. Pruedhomme, *C. R. Acad. Sci., Ser. C,* **271**, 1073 (1970).

(25) Hk. Muller-Buschbaum and R. von Schenck, *Z. Anorg. Allg. Chem.,* **377**, 70 (1970).

observed distance of 2.44 Å. Similarly, the Pt-O distance of 1.99 Å compares well with Pt^{2+} (IV) + (O^{2-}) = 2.00 Å. The sp^2 hybridization of the oxygen atoms accounts readily for the planar-triangular bonding to Pt. The Pt-Pt distance indicates metallic bonding (Pt-Pt in Pt metal is 2.80 Å).

In $CaPt_2O_4$ the situation seems to be more complex. The Pt atoms are not equidistant but slightly paired, although we presume that all the bonds have metallic character. The Ca^{2+} ions again fit very well in the oxygen channels, as shown by the Ca-O bond length of 2.48 Å (the sum of the ionic radii is 2.52 Å). The oxygen coordination around the Pt is slightly distorted from square planarity, but hardly significantly so. The Pt lies 0.15 (5) Å from the plane defined by the four-coordinated oxygen atoms. As in the general bronze structure, chains of alternating Ca and O atoms run diagonally through the crystal.

Most unusual is the coordination of Pt around oxygen. It was this feature that prompted us to calculate the difference Fourier synthesis and to vary the Pt occupancy factor (as described above) in order to see if some electron density might be found in the channels of the structure. The resulting bonding shows each oxygen atom connected to two platinum atoms, with the angle between them close to 120° [110 (3)°]. This suggests that some electron density centered on the oxygen is pointing toward the position where Pt would be found in the bronze structure. Although such bonding for oxygen is not uncommon (*e.g.*, H_2O) it is highly unusual in a metal oxide. As mentioned before, metallic bonding between the platinum atoms is found in both $Cd_{0.3}Pt_3O_4$ and $CaPt_2O_4$. We are currently investigating some of the physical properties of these and other bronzes in order to look for evidence of metallic behavior in these materials. The results of this study together with details on the preparation and catalytic behavior of the bronzes will be the subjects of future publications.

Registry No. $CaPt_2O_4$, 39394-82-6; $CdPt_3O_4$, 39394-83-7; $Cd_xPt_3O_4$, 39394-68-8.

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Solid Coordination Compounds of Alkali Metal Salts with a Neutral Aromatic Amine.[1] I. Molecular Structure and Bonding

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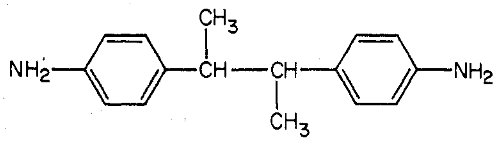
Uni-univalent metal salts, including alkali metal salts, are precipitated from aqueous solution by complexation with racemic *p,p'*-diamino-2,3-diphenylbutane. The stoichiometry and infrared and solution properties of these compounds are presented and discussed in terms of coordination compounds in which the metal ion is octahedrally coordinated by six amino nitrogen atoms to give an infinite three-dimensional polymeric structure. Evidence is presented for strong metal ion-amino nitrogen bonding as well as interaction between the anion and amino hydrogens. Both of these attractive interactions are attributed to ion dipole forces. Evidence is also presented which strongly indicates that there is little anion-cation interaction.

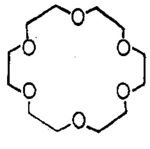
Introduction

In a previous communication,[1] we reported initial results on the precipitation of simple alkali metal salts such as sodium chloride from aqueous solution by complexation with racemic *p,p'*-diamino-2,3-diphenylbutane (I). The stoichiometry, constant composition, and infrared spectrum of the NaCl adduct with I was interpreted in terms of a structure in which six nitrogen atoms from six amino groups are octahedrally coordinated about the sodium. This is unusual since of the alkali metals only lithium salts are known to form isolable coordination compounds with nitrogen donor ligands. The more stable are those where the ligand is ammonia, and replacement of ammonia with amines decreases their stability. It is therefore surprising that I, a weakly basic and bulky aromatic amine, can exhibit bonding with sodium.

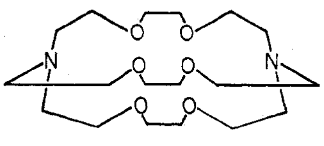
Unlike nitrogen, there are many examples of oxygen donor ligands which effectively coordinate with alkali metal cations. Some notable recent examples are the macrocyclic ethers (crown ethers) (II)[2] and the macroheterobicyclics (cryptates) (III).[3] Subsequent to our initial report methylenedianiline (IV), a closely analogous compound of I, was reported to form isolable compounds with alkali metal salts.[4]



I



II



III

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[1] (a) A preliminary account of a portion of this work has been reported: N. P. Marullo and R. A. Lloyd, *J. Amer. Chem. Soc.*, 88, 1076 (1966). (b) Abstracted in part from the Master's thesis of R. A. Lloyd and Ph.D. thesis of G. T. Cochran, Clemson University, 1967.

[2] D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, 94, 4024 (1972), and references cited therein.

[3] J. M. Lehn and J. P. Sauvage, *Chem. Commun.*, 440 (1971), and references cited therein.

[4] T. C. Shields, *Chem. Commun.*, 832 (1968).