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Structure and Properties of $Ni_{0.25}Pt_3O_4$. A New Platinum Bronze

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Received March 17, 1972

The first single-crystal preparation, structure determination, and electrical conductivity measurements of a platinum–metal bronze are described. The nickel–platinum bronze $Ni_{0.25}Pt_3O_4$ has a cubic structure with a = 5.61 (2) Å and crystallizes in space group $Pm3n$ or $P\bar{4}3n$, with two formula units per unit cell. The structure was solved using three-dimensional X-ray data, collected by counter methods. Refinement by full-matrix least-squares methods gave a final R factor of 5.6% on F for the 18 independent reflections. The structure can be described in terms of a filled β-tungsten type, where the "filling" oxygen atoms are in square-planar coordination around the platinum atoms. Nonintersecting chains of Pt atoms run parallel to all three cubic axes. The short Pt–Pt distance of 2.80 (1) Å and the electrical resistivity data indicate extensive metallic bonding along the chains. The Ni atoms are situated in channels, each Ni atom being very weakly bonded to eight oxygen atoms.

Introduction

Interest in platinum–metal bronzes arises from their unusual structure, characterized by isolated Pt–Pt chains extending parallel to the three cubic axes. It is also of interest to determine how far one can compare these bronzes with the well-known tungsten bronzes. Furthermore, as platinum is extensively used as an inert material in high-temperature work, one would like to know under which conditions it will react with the surroundings and what the products are.

The first member of this family to be synthesized was $Na_xPt_3O_4$ ($1 \geq x \geq 0$) as early as 1877.[2a] Wöhler,[2b] Busch,[3] Waser and McClanahan,[4] Galloni and Busch,[5] Ariya, Morozova, Markevich, and Reikhardt,[6] Scheer, van Arkel, and Heyding,[7] Asanov and Shishakov,[8] Shishakov and Andrushchenko,[9] and Muller and Roy[10] all reported the synthesis of a member of the $Na_xPt_3O_4$ group. Among the other bronzes known today are $Mg_xPt_3O_4$, $Ni_xPt_3O_4$, and the palladium bronzes $NaPd_3O_4$,[7,11] $CaPd_3O_4$,[12,13] $CdPd_3O_4$,[12] and $SrPd_3O_4$.[12,13b]

Considerable controversy has arisen over the stoichiometry,[8,9] structure,[10] and electrical properties[4a,13a,14] of these oxides. Muller and Roy[10] have discussed in detail the discrepancies in the structural results. Subsequently, Sukhotin, *et al.*,[15] have also shown that the Pt and O arrangement in Pt_3O_4 is the same as that in $Na_xPt_3O_4$.[4a]

Because of the highly unusual structure, derived from powder data, by Waser and McClanahan[4a] for $Na_xPt_3O_4$ and because of the fact that for the first time a platinum bronze, $Ni_xPt_3O_4$, was obtained in single-crystal form, we decided to examine both the structure and the electrical properties of $Ni_xPt_3O_4$.

Waser and McClanahan[4a] concluded from their powder data that $Na_xPt_3O_4$ belongs to the space group $Pm3n$ (O_h^3) and that infinite Pt–Pt chains extend parallel to all three cubic axes. They placed the platinum atoms in position 6c ($^1/_4$, 0, $^1/_2$ Ↄ), the oxygen atoms in 8e ($^1/_4$, $^1/_4$, $^1/_4$ Ↄ) and the Na atoms in 2a (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$). Since the resultant Pt–Pt distance was only slightly longer than that of 2.77 Å found in the metal, they expected metallic conduction. Their measurements indicated ionic conductivity with a room-temperature resistivity of $\sim 10^4$ ohms cm.

Wnuk, *et al.*,[13a] found that $CaPd_3O_4$ behaves as a p-type semiconductor with a resistivity of ~ 3 ohms cm at liquid nitrogen temperature. Both these measurements were done on polycrystalline material and thus may be inconclusive.

In the course of an investigation of some ternary oxides of Pt[16] while trying to prepare $PtNiO_2$, we obtained crystals of $Ni_xPt_3O_4$ which we suspected had the $Na_xPt_3O_4$ structure. In this paper we report the synthesis, electrical resistivity, and single-crystal structure determination of $Ni_{0.25}Pt_3O_4$.

Experimental Section

Reagent grade $PtCl_2$ (Matthey-Bishop), NiO (Vitro Laboratories), and $KClO_3$ (Fisher) were used as starting materials. Typically, 0.78 g of $PtCl_2$, 0.21 g of NiO, 0.50 g of $KClO_3$, and 1 ml of H_2O were sealed in a Pt tube, placed in a pressure vessel, and heated to 700° under 3000 atm for 24 hr. The product consisted of a mixture of (a) blue-black crystals, (b) yellow-green transparent platelets (probably $PtCl_2$), and (c) brown powder. Most of the black crystals were found adhering to the walls of the Pt tube. They generally had an irregular shape, but well-defined square or rectangular faces 0.05–0.25 mm on an edge could be recognized. A small fraction of the crystals were approximately cubic. Although there was insufficient material for a complete wet chemical analysis, emission spectrographic analysis of a small portion of the sample indicated the presence of 0.5–2.0% Ni. Preliminary X-ray precession patterns showed the crystal to be cubic with $a = 5.61 \pm 0.03$ Å and space group extinctions hhl, $l = 2n + 1$. From the similarity to $Na_xPt_3O_4$, the composition of the crystals was assumed to be $Ni_xPt_3O_4$ where x from the spectrographic analysis was 0.06–0.23.

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

(3) R. H. Busch, *Z. Naturforsch. A*, **5**, 130 (1950).

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

(5) R. E. Galloni and R. H. Busch, *ibid.*, **20**, 199 (1952).

(6) S. M. Ariya, M. P. Morozova, G. S. Markevich, and A. A. Reikhardt, *Sb. Statei Obshch. Khim., 1953*, **1**, 76 (1953); see also S. M. Ariya, M. P. Morozova, and A. A. Reikhardt, *J. Gen. Chem. USSR*, **23**, 1521 (1953).

(7) J. J. Scheer, A. E. van Arkel, and R. D. Heyding, *Can. J. Chem.*, **33**, 683 (1955).

(8) U. A. Asanov and N. A. Shishakov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **2**, 205 (1961).

(9) N. A. Shishakov and N. K. Andrushchenko, *Russ. J. Phys. Chem.*, **35**, 780 (1961).

(10) O. Muller and R. Roy, *J. Less-Common Metals*, **16**, 129 (1968).

(11) R. Scholder, K.-G. Malle, B. Triebskorn, and H. Schwarz, *Z. Anorg. Allg. Chem.*, **364**, 41 (1969).

(12) O. Muller and R. Roy, *Advan. Chem. Ser.*, **98**, 28 (1971).

(13) (a) R. C. Wnuk, T. R. Touw, and B. Post, *IBM J. Res. Develop.*, **8** (4), 185 (1964); (b) H. D. Wasel-Nielen and R. Hoppe, *Z. Anorg. Allg. Chem.*, **375**, 209 (1970).

(14) M. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

(15) A. M. Sukhotin, E. A. Gankin, Y. D. Kondrashov, Y. A. Omel'chenko, and B. Y. Shal'man, *Zh. Neorg. Khim.*, **16**, 3190 (1971); *Chem. Abstr.*, **76**, 53818 (1972).

X-Ray powder diffraction data were obtained on a Guinier camera as described earlier.[16a] Because $Na_xPt_3O_4$ had been suspected to exhibit metallic conductivity, the electrical resistivity was measured as a function of temperature by a conventional four-probe method described earlier.[16b]

Structure Determination

The crystals of $Ni_{0.25}Pt_3O_4$ were in the form of small dodecahedra truncated by {100} faces. A crystal of approximate dimensions 0.01 × 0.015 × 0.015 cm was mounted and used for space group determination. Zero and upper level Weissenberg photographs and precession photographs, along the main axes as well as along the diagonals, confirmed Waser and McClanahan's original space group determination: $O_h{}^3$ ($Pm3n$) or $T_d{}^4$ ($P\bar{4}3n$). The only systematic absences observed were hhl, $l = 2n + 1$.

A slightly smaller crystal, with a more regular habit, was mounted for counter data collection on a Picker FACS1 diffractometer, in a random orientation 6° off the $1\bar{1}\bar{5}$ axis. The crystal faces were indexed by optical goniometry and these results were used for orientation on the diffractometer. The dimensions of this data crystal were 0.0105 × 0.0074 × 0.0070 cm, determined by microscopy, using a traveling eyepiece. The crystal had 11 regular faces and was irregularly chopped off at one side.

Because trial ω–2θ and ω scans showed large mosaicity, up to 4° in ω, data were collected using the ω-scan method.[17] A total of 747 reflections were collected at a scan rate of 0.25°/min and a scan range of 4° in ω. Background was measured by stationary counting at both ends for 40 sec each. A graphite monochromator, with the (002) plane in diffracting position, was used to obtain monochromatic Mo Kα radiation. A takeoff angle of 5° was found to be suitable.[18]

The relatively strong 400, 040, and 004 reflections were used as internal standards and collected every 50 reflections. No significant change in intensity of the standards was observed.

Reflections were measured for $-5 \leq h,k,l \leq 5, 6° < 2\theta < 40°$. Since the number of variables to be determined was thought to be small, no further measurements were made. Among the reflections measured in this way, 138 were less than their σ, 60 were between σ and 2σ, and 44 were between 2σ and 3σ, where σ was estimated from counting statistics. Thus there were 505 members of the 22 independent forms for which $I > 3\sigma(I)$.

Absorption Correction

Because μ, the linear absorption coefficient, is 1260 cm^{-1} for $Ni_{0.25}Pt_3O_4$, for Mo Kα radiation, a reliable correction for absorption is mandatory. Several trial runs with Hamilton's GONO9 program, using various increasing isometric grids for numerical evaluation of the absorption correction, gave unsatisfactory results (*i.e.*, no convergence to a limiting value was observed, if the number of grid points was increased). A local version of Coppens' DATAPP[19] program, which uses a Gaussian grid instead, was used and reasonable results were obtained, using a 12 × 12 × 32 grid. These results were checked for some reflections, using a 32 × 32 × 32 grid, and later, against the results obtained with our version of Tompa's[20] analytical absorption method. As various difficulties and inconsistencies were encountered with several programmed versions of this method, our analytical program was tested as described elsewhere.[21]

To check the accuracy of the crystal measurements, a computer drawing was made of the model of the crystal, as put into the absorption correction programs. The transmission varied from ~0.007 to 0.06 for different reflections.

After applying Lorentz, polarization, and absorption corrections, the data were averaged (reflections with $I > 3\sigma$ only).[22] In this way 22 independent reflections were obtained. This small number is, however, more than sufficient, since the structure is a highly symmetrical one. These reflections were weighted, using the relation $\sigma(F) = 0.1F\sqrt{9/\mathrm{NO}}$, where NO is the number of reflections per averaged reflection. This relation was used because of the poor quality of the crystal and the relatively wide scan range, which made a σ proportional to the intensity the most reasonable one.

Refinement of Structure

The Pt atoms were placed in the positions proposed by Waser and McClanahan for $Na_xPt_3O_4$. Refinement of the scale factor and the Pt isotropic temperature factor only gave an agreement factor $R_F = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 13.7%. A difference Fourier map failed to show electron density at any reasonable positions for the oxygen atoms. Adding the oxygen atoms to the refinement in the positions of O in $NaPt_3O_4$ did not improve the agreement factor. The Ni atoms, however, were readily located from the difference Fourier map, at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$, *i.e.*, the positions of Na in $NaPt_3O_4$. The value of x in the formula $Ni_xPt_3O_4$ was calculated from this difference Fourier to be 0.23.

After determination of the Pt and Ni positions, it was obvious that the oxygen atoms had to be in the same positions as in $NaPt_3O_4$, as no other chemically reasonable positions are available in either of the two possible space groups.

In order to locate the oxygen atoms, a refinement was attempted using only those reflections that have oxygen contributions (*i.e.*, h,k,l all even). In this way, six independent reflections were left and used to refine the Pt temperature factor only. Again, however, a difference Fourier map failed to show any reasonable oxygen electron density.

At this point, we decided to re-collect part of the data, using a wider scan range. Inspection of the intensity plots of the first data set showed that the 4° scan range in ω had not always been wide enough, especially for the stronger reflections. This we attribute to the high anisotropic mosaicity of the crystal, as careful analysis of photographic data from the data crystal convinced us that the crystal is indeed single.

In order to take into account this mosaicity and to guarantee inclusion of the complete reflection intensity envelope, data were re-collected in the following way. Triclinic lattice parameters were used to calculate setting angles. These parameters were obtained by least-squares refinement of the observed setting angles of the complete {222} family, where as ω value the center of the intensity envelope was used. In this way the following "working" lattice parameters were obtained: $a = 5.5064$ Å, $b = 5.7634$ Å, $c = 5.7075$ Å, $\cos \alpha = 0.0591$, $\cos \beta = 0.0561$, $\cos \lambda = 0.0064$. Furthermore a wider scan range, 9° in ω, centered on $\omega = 0°$, was determined to be sufficient, so that every peak fell within this range. The scan rate was 1°/min and the other experimental conditions were identical with those of the first set. All the 144 reflections that were re-collected were larger than 3σ. These data were now combined with those reflections of the original data set, which had been scanned completely and contained oxygen contributions. We now had 184 members of 23 independent forms. After correction for polarization and absorption, using our analytical program, inspection showed that some reflections were affected considerably by surface scattering from the irregular side of the crystal (approximately parallel to the $\bar{1}1\bar{1}$ face). These were excluded from the averaging process leaving 18 independent reflections.

After adjustment of scale factors, refinement of the combined data set, with only Pt atoms, gave an R_F of 11.3% and a $wR_F = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$ of 12.5% where $w = 1/\sigma^2$ and σ of averaged data is the same as defined earlier. Using both Pt and O an R_F of 7.9% and wR_F of 9.1% were obtained. In the final refinement all atoms were included, and the Pt and O temperature factors as well as the Ni occupancy were varied.

Next, the temperature factor of Pt was refined anisotropically, taking into account the limitations imposed on the β's by the site symmetry of the Pt position ($\beta_{11} = \beta_{22}$, $\beta_{12} = \beta_{13} = \beta_{23} = 0$).

An attempt was made to refine the structure in the noncentrosymmetric space group $P\bar{4}3n$. The results obtained, as shown in Table II and Figure 1, were, however, not conclusive. In $P\bar{4}3n$, oxygen would be in position 8e (x, x, x; $\bar{x}$, $\bar{x}$, $\bar{x}$↻) with site symmetry 3 instead of 32 as in $Pm3n$. Madelung energy calculations and oxygen-site potential evaluations show a rather shallow minimum around x (oxygen positional parameter in $P\bar{4}3n$) = 0.25 (Figure 2).

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[16] (a) R. D. Shannon, D. B. Rogers, and C. T. Prewitt, *Inorg. Chem.*, **10**, 713 (1971); (b) D. B. Rogers, R. D. Shannon, C. T. Prewitt, and J. L. Gilsson, *ibid.*, **10**, 723 (1971).

[17] U. W. Arndt and B. T. M. Willis, "Single Crystal Diffractometry," Cambridge University Press, London, 1966, p 265.

[18] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[19] P. Coppens in "Crystallographic Computing," F. R. Ahmed Ed., Munksgaard, Copenhagen, 1970, p 255.

[20] J. deMeulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

[21] D. Cahen and J. A. Ibers, *J. Appl. Crystallogr.*, in press.

[22] Besides several local ones, the following programs were used for a CDC 6400 computer: ORFFE, of Busing and Levy; a local version of their ORFLS; Johnson's ORTEP II; Zalkin's FORDAP; and Piken and van Gool's lattice energy program.

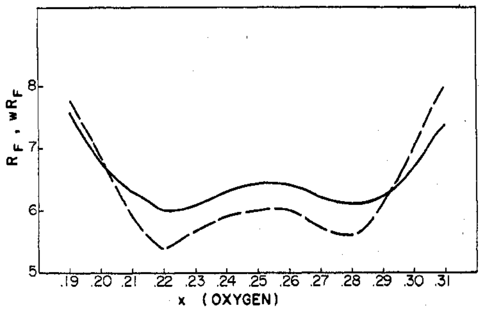

Figure 1.—R_F (– – –) and wR_F (——) as a function of the positional parameter of the oxygen atom.

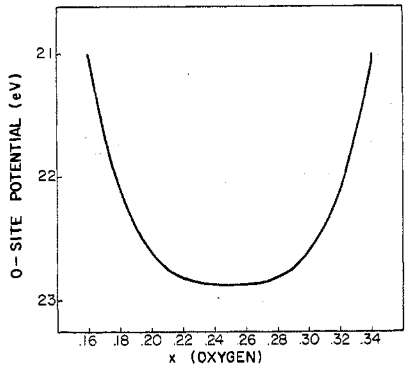

Figure 2.—Electrostatic oxygen-site potential as a function of the oxygen positional parameter.

A possible explanation for shifting the oxygens away from the $^1/_4$, $^1/_4$, $^1/_4$ position, which results in a distortion of the square-planar coordination around Pt, may be found in orbital symmetry considerations. If we consider Pt as formally $d^{7.7}$, orbital symmetry[23] predicts a change of site symmetry from D_{4h} to D_{2d} or T_d, as is the case upon excitation of a d^8 complex such as $PtCl_4^{2-}$. Although such an argument can be made for the noncentrosymmetric structure, we prefer the more symmetric model, especially in view of the poor quality of the data.

A final difference Fourier map shows no peak with a height greater than half of that of an oxygen peak.

Table I compares the observed and calculated structure amplitudes for the centrosymmetric structure. Positional and thermal parameters and occupancy factors are given in Tables II and III. Important interatomic distances are given in Table IV.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES IN ELECTRONS FOR MODEL A (CENTROSYMMETRIC)

hkl	F_o	F_c	*hkl*	F_o	F_c
000		536.0	321	103.3	94.7
110	127.7	123.6	330	77.8	74.1
200	91.0	91.6	332	69.8	74.8
200	81.2	91.6	411	76.6	76.4
210	238.5	240.4	420	65.5	65.0
211	132.9	125.5	421	154.0	147.6
220	65.8	68.9	422	52.3	50.0
220	73.8	68.9	431	70.2	62.6
222	331.1	301.1	432	117.4	120.4
310	97.0	92.7	520	95.5	118.9
320	162.9	182.7			

Scattering factors for Pt^0, Ni^0, and O^0 were taken from Cromer and Waber.[24] Anomalous dispersion terms were taken from Cromer and Liberman.[25]

TABLE II

RESULTS OF FINAL REFINEMENTS

	Model A	Model B	Model C
Space group	*Pm3n*	$P\bar{4}3n$[d]	$P\bar{4}3n$[d]
β_{11}(platinum)	0.14 (3)	0.14 (3)	0.14 (3)
β_{33}(platinum)	0.16 (5)	0.17 (4)	0.16 (5)
Nickel occupancy	0.24 (8)	0.26 (8)	0.24 (12)
B(nickel),[b] Å^2	2.0 (4.0)	4.6 (3.0)	3.3 (6.0)
x(oxygen)	0.25[a]	0.22 (1)	0.28 (1)
B(oxygen),[b] Å^2	3.2 (3.4)	1.0 (2.8)	−0.72 (2.7)
R_F[c]	5.6	5.4	5.7
wR_F[c]	6.3	6.0	6.0

[a] Not varied in the refinement. [b] Neither the oxygen nor the nickel temperature factor could be determined accurately in the platinum-dominated structure. B(Ni) and B(O) were strongly correlated with Ni occupancy and x(O), respectively (correlation coefficients: ~0.8). [c] As defined in text. [d] Models B and C are equivalent structures. Differences between them are due to the presence of anomalous scatterers, Pt and Ni.

TABLE III

POSITIONAL PARAMETERS, SITE SYMMETRY, AND WYCKOFF NOTATION OF ATOMS IN $Ni_{0.25}Pt_3O_4$

Atom	*x*	*y*	*z*	Site symmetry	Wyckoff notation	Occupancy
Platinum	$^1/_4$	0	$^1/_2$	$\bar{4}2m$	6c	6
Oxygen	$^1/_4$	$^1/_4$	$^1/_4$	32	8e	8
Nickel	0	0	0	*m*3	2a	0.5 (25%)

TABLE IV

INTERATOMIC DISTANCES (Å) IN $Ni_{0.25}Pt_3O_4$

	Centric model[a]		Noncentric model[b]	
Pt–O	1.983 (7)	4[d]	2.00 (2)	4
	3.43 (1)	4	3.31 (5)	4
Ni–O	2.428 (9)	8	2.2 (1)	4
			2.7 (1)	4
O–O	2.80 (1)	6	2.84 (4)	6
Pt–Pt[c]	2.80 (1)	2		
	3.43 (1)	8		
Pt–Ni[c]	3.13 (1)	12		

[a] As all atoms are in special positions in the centric model, errors in the interatomic distances are due only to errors in the lattice parameter. [b] x(oxygen) = 0.22 (1). [c] Unaffected by variation in oxygen positional parameter. [d] Number of equivalent distances.

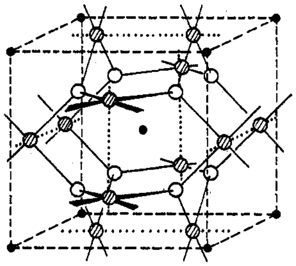

Figure 3.—The arrangement of Pt and O atoms in $Ni_{0.25}Pt_3O_4$ in terms of a three, four-connected net. The Pt atoms are drawn as shaded circles; the O atoms as open ones. Pt–Pt bonds are dotted. Ni atoms are drawn as solid dots (after Wells[27]).

Using the anomalous scattering terms, the difference between the centro- and noncentrosymmetric models, as calculated for *hkl* and $\bar{h}\bar{k}\bar{l}$, was found to be too small to be observed ($<\sigma$, σ from counting statistics).

Discussion

The MPt_3O_4 structure seems to be unique to this family of compounds. It can be described as a filled β-W structure (Type A15),[26] where the oxygen atoms provide the "filling."

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[23] R. G. Pearson, *Chem. Phys. Lett.*, **10**, 31 (1971).

[24] "International Tables for X-Ray Crystallography," Vol. IV, W. Hamilton and J. A. Ibers, Ed., Kynoch Press, Birmingham, England, in press.

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

[26] H. Hartmann, F. Ebert, and O. Bretschneider, *Z. Anorg. Allg. Chem.*, **198**, 116 (1931).

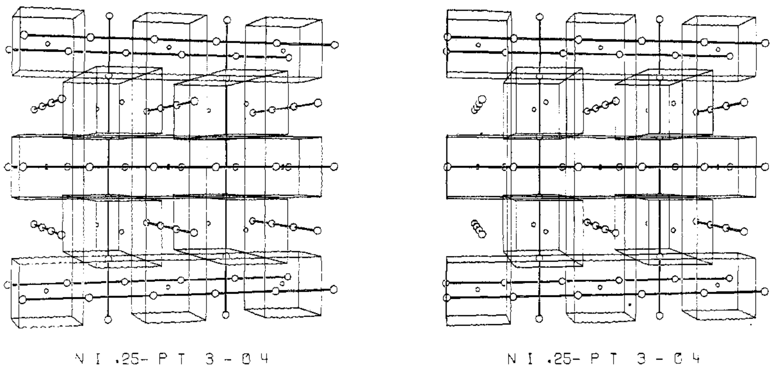

Figure 4.—Stereoscopic pair drawing of the $Ni_{0.25}Pt_3O_4$ structure in terms of oxygen coordination cubes around Ni, with chains of Pt atoms running between them.

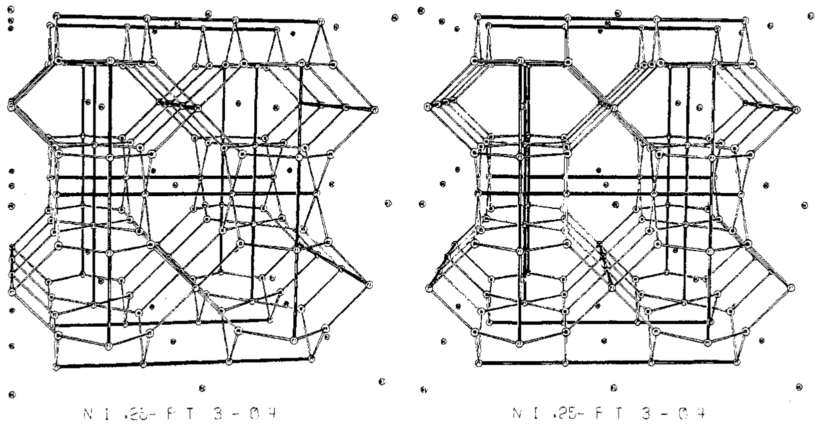

Figure 5.—Stereoscopic pair drawing of the $Ni_{0.25}Pt_3O_4$ structure showing all bonded interactions and the channels in which the Ni atoms are situated.

Wells[27] classified the structure as the only member of a class, where one has three-dimensional nets, in which three-connected points (oxygen) are linked only to four-connected points (platinum) and *vice versa* (Figure 3).

The short Pt–Pt distance of 2.80 Å, only slightly greater than that in the metal, which occurs in the chains of Pt atoms running parallel to the crystal axes, reminds one of the same phenomenon in one dimension, as exhibited by partially oxidized Pt complexes.[28]

In terms of coordination polyhedra, one can describe the structure as being built up from cubes of O around Ni, sharing vertices (Figure 4). Between these cubes run the chains of Pt. Thus it seems improbable that the 2a (Ni) position would ever be empty. Refinement of Muller and Roy's[10] data for Pt_3O_4 showed that better agreement was obtained if some electron density was put in this position. In this case one could indeed have, as suggested by Shishakov,[9] *et al.*, HPt_3O_4 or perhaps $(H_2O)_xPt_3O_4$ as is suggested by Wöhler's[2b] original analytical data.

The formal oxidation state of Ni is not obvious from the stoichiometry. Magnetic susceptibility measurements show a weak paramagnetism, nearly temperature independent, thereby excluding Ni^{III}. From comparison with $Na_xPt_3O_4$ and several partially oxidized Pt complexes,[28] one could assign Pt the formal oxidation number $^7/_3$ which would imply the presence of Ni^{IV}.

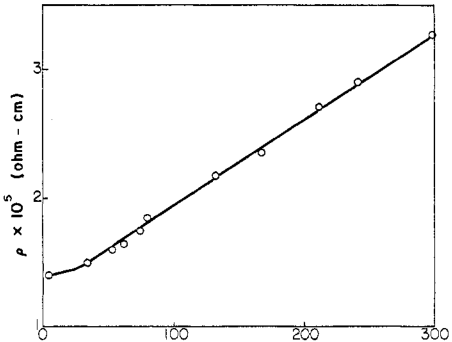

Figure 6.—Specific resistivity of $Ni_{0.25}Pt_3O_4$ as a function of temperature.

As the Ni is sitting in a hole, the Ni–O bond distances do not provide any clues. In the noncentric model (Table IV) only the short Ni–O distance suggests any bonding. In the centric model the Ni is "swimming" in the channel (Ni–O = 2.43 Å) (Figure 5). A normal Ni^{II}–O bond would be ~2.0 Å.

The electrical behavior is explained by the short Pt–Pt distance. Figure 6 shows the typical metallic behavior exhibited by single crystals of $Ni_{0.25}Pt_3O_4$. The room-temperature resistivity is 3.3×10^{-4} ohm cm. The relatively low ratio (2.3) of the resistivity at room temperature to that at liquid helium temperature probably indicates a large number of impurities.

The observed conductivity places $Ni_{0.25}Pt_3O_4$ in class IIIb of mixed-valence compounds.[14] Robin and Day pointed out that $NaPt_3O_4$, on the basis of its

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(27) A. F. Wells, *Acta Crystallogr.*, **18**, 894 (1965).
(28) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).

structure, belonged to this class but that then its electrical behavior (ionic conductivity) was not explained. From the structure it seems that both types of conductivity should take place. Figure 5 shows the channels through which the Ni ions can move. However, because of differences in order of magnitude of electronic and ionic transference numbers, any ionic conductivity present is probably obscured.

Acknowledgments.—We wish to thank J. L. Gillson for making the resistivity measurements and J. E. Whitney, Mrs. C. M. Foris, and Mrs .J. E. Hall for assistance with precession and Guinier photographs. This work was supported at Northwestern University by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center.

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Crystallographic Determination of Stereochemistry for the Triclinic and Tetragonal Modifications of a Bis-Bidentate Metal Complex, Bis(*N-tert*-butylpyrrole-2-carbaldimino)copper(II)[1]

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Received February 24, 1972

The crystal structures of the triclinic and tetragonal modifications of a bis-bidentate copper complex, bis(*N-tert*-butylpyrrole-2-carbaldimino)copper(II), have been determined from three-dimensional single-crystal X-ray diffraction data which were measured photographically. The triclinic crystals belong to space group $P\bar{1}$ (C_i^1, No. 2) with a = 7.49 (1) Å, b = 11.26 (2) Å, c = 11.73 (2) Å, α = 81° 41′ (15′), β = 89° 38′ (15′), γ = 76° 16′ (15′), and Z = 2. The tetragonal crystals possess $P4_12_12$ (D_4^4, No. 92) symmetry with a = 9.89 (2) Å, c = 19.08 (2) Å, and Z = 4. Both structures were solved by heavy-atom techniques and refined by the full-matrix least-squares method. The final reliability indexes are R_F = 0.069 and R_{wF} = 0.056 (1089 reflections) for the triclinic form and R_F = 0.083 and R_{wF} = 0.070 (504 reflections) for the tetragonal modification. The molecule ideally conforms to C_2 symmetry in the triclinic cell and possesses crystallographic C_2 symmetry in the tetragonal cell. The two molecular structures are similar, and the coordination around the copper atom may be described as distorted tetrahedral, with the dihedral angles of 61.3 (4) and 60.1 (9)° for the triclinic and tetragonal modifications, respectively, between the two coordination planes each defined by an MN_2 moiety. In each case, the M–N(pyrrole) bond distance [2.054 (8) Å for the former and 2.044 (14) Å for the latter] is approximately 0.12 Å longer than the M–N(azomethine) bond distance [1.939 (8) Å for the former and 1.922 (15) Å for the latter]. The interchelate N–Cu–N "bite" angles are 84.7 (4) and 85.4 (6)°, and the N···N bite distances are 2.69 (1) and 2.69 (2) Å for the triclinic and tetragonal modifications, respectively.

Introduction

Various four-coordinated copper(II) complexes, particularly those of salicylaldimines, have been reported and many of them have been subjected to two- or three-dimensional X-ray analyses.[3–11] The structural results reveal that most of these complexes are effectively square planar with only a few complexes exhibiting configurations which may be described as flattened or distorted tetrahedral. As an example, bis(*N*-isopropylsalicylaldiminato)copper(II),[9] first reported as having a structure nearly isomorphous with that of the Ni(II) analog[12] whose structure was later determined as pseudotetrahedral,[13] has been shown to possess a dihedral angle of 59.7° between the two coordination planes each defined by Cu, N, and O atoms. Unlike the *n*-butyl analog, which is planar,[10] the *tert*-butyl analog[11] also has a distorted tetrahedral configuration with a dihedral angle of 53.6° between the two coordination planes defined as above. Recently, the molecule of bis(2,3-bipyridylamine)copper(II)[14] has also been shown to have a dihedral angle of 55.6° between the two CuN_2 coordination planes. It has been well recognized that steric interaction between the ligands is an important factor for a copper(II) complex to exhibit the configuration which deviates from planarity to varying degrees.

In 1966, Holm and his coworkers[15] reported that they had synthesized bis(*N-tert*-butylpyrrole-2-carbaldimino)metal(II) complexes where metal = cobalt, nickel, copper, and zinc (with the pyrrole–CH–N–*t*-Bu moiety as a ligand) and made extensive investigations of their chemistry. Structural analyses

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(1) (a) Research jointly supported by the Wisconsin Alumni Research Foundation at the University of Wisconsin and by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp. (b) Presented in part at the Winter Meeting of the American Crystallographic Association, Tulane University, New Orleans, La., March 1–5, 1970.

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(3) (a) For a complete coverage up to about Dec 1964 see R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 110 (1966); (b) for the latest review on the stereochemistry of bis(chelate)metal(II) complexes, see R. H. Holm and M. J. O'Conner, *ibid.*, **14**, 241 (1971).

(4) To supplement in part the references given in ref 3a, the results of three-dimensional X-ray structural determinations of the bis(*N*-alkylsalicylaldiminato)copper(II) series alone have appeared in the literature since 1965 for alkyl = H,[5] CH_3,[6] C_2H_5,[7] *n*-propyl,[8] isopropyl,[9] *n*-butyl,[10] and *tert*-butyl.[11]

(5) E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 680 (1966).

(6) D. Hall, S. V. Sheat, and T. N. Waters, *ibid.*, 460 (1968).

(7) (a) E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters *ibid.*, 251 (1967); (b) G. R. Clark, D. Hall, and T. N. Waters, *ibid.*, 2808 (1969).

(8) G. Bombieri, C. Panattoni, E. Forsellini, and R. Graziani, *Acta Crystallogr., Sect. B*, **25**, 1208 (1969).

(9) P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, **88**, 277 (1966).

(10) D. Hall, R. H. Summer, and T. N. Waters, *J. Chem. Soc. A*, 420 (1969).

(11) T. P. Cheeseman, D. Hall, and T. N. Waters, *ibid.*, 685 (1966).

(12) L. Sacconi and P. L. Orioli, *Ric. Sci.*, **32**, 645 (1962).

(13) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *Acta Crystallogr.*, **17**, 1159 (1964).

(14) J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc. A*, 1371 (1971).

(15) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).