JOURNAL OF SOLID STATE CHEMISTRY 27, 389–396 (1979)

Crystal and Molecular Structure of the Linear Metal–Chain Semiconductor Bis(1,2-benzoquinonedioximato)platinum(II), $Pt(bqd)_2$*

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Received May 1, 1978

The full, three-dimensional crystal and molecular structure of the title compound has been determined by conventional single-crystal X-ray diffraction. The data were collected at room temperature by counter methods with a Syntex $P2_1$ four circle, computer controlled diffractometer using graphite monochromated Mo$K\alpha$ radiation and $\theta/2\theta$ scans ($0° < 2\theta \leq 70°$). A $0.35 \times 0.25 \times 0.15$ mm crystal was utilized and yielded the following crystal data: $PtC_{12}H_{10}N_4O_4$, mol wt = 469.33, orthorhombic space group Ibam (D_{2h}^{26}), cell constants $a = 20.68(9)$Å, $b = 9.743(3)$Å, $c = 6.346(2)$Å, $V = 1279(1)$Å^3; $Z = 4$, $d_{calc} = 2.44$ g/cm^3. The structure was refined by full-matrix least-squares methods using 758 independent reflections ($I > 3.5\sigma(I)$) to a final $R = 5.2\%$ for all nonhydrogen atoms. The lattice is built up of neutral, completely coplanar $Pt(bqd)_2$ complexes with the Pt(II) core at the molecular center of symmetry. The four N atoms of the bidentate chelating ligands are arranged in a rectangle around the central metal ion at a distance M–N = 1.99 Å. The flat complex units are stacked equidistantly one on top of the other along the c-axis with the molecular planes disposed strictly perpendicular to the stacking direction. The nearest neighbors within a stack are staggered by an angle of 93°. The Pt(II) sites are aligned in "infinite" straight chains with a regular Pt–Pt contact of only 3.173 Å ($c/2$), the shortest observed so far in unoxidized 1,2-dionedioximates of transition metal ions. This unusually short intermetallic separation is most reasonably linked to the large *ligand-induced nephelauxetic effect* of the Pt d^8-shell.

Introduction

X-ray structure determinations of various square-planar, linear metal–chain complexes of general formula $M(bqd)_2$ ($M = Ni^{2+}, Pd^{2+}, Pt^{2+}$; $bqd^- =$ ion of 1,2-benzoquinonedioxime, bqdH) have been published recently (*1–3*). The chemical and most relevant physical properties (such as electrical, optical and elastic) of these stacked, pseudo one-dimensional compounds have been reported as well (*4–5*).

The research has been motivated by the search for new one-dimensional electronic materials similar to the partially oxidized tetracyanoplatinates (*6–8*), with the ultimate goal of achieving a high temperature superconductor according to the hypothetical excitonic model of Little (*9*). Although the quasi-insulating d^8 complexes, $Ni(bqd)_2$ and $Pd(bqd)_2$, could be partially oxidized with molecular iodine (*10*), the resulting solids (containing chains of triiodide ions, I_3^- (*11, 12*) did not show any obvious evidence for the expected one-dimensional "metallic" behavior (*5, 13*). This failure is presumed to be due to the degree of partial oxidation in the solids which is too small to effect a

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* This work was supported by the National Science Foundation, Grant No. DMR-76-82087-A01, and the Office of Naval Research, Contract No. NOOO14-77-C-0631.

0022–4596/79/030391–08$02.00/0

Printed in Great Britain

"metallic" density of states within the d_{z^2} conduction bands (*4*). Nevertheless, the slight partial oxidation resulted in an increase of the dc electrical conductivity (*13, 14*) by a factor of at least 10^6.

Preliminary examination by X-ray diffraction (*15*) has shown that $Pt(bqd)_2$ crystallizes in stacks, isostructurally with the analogous α-$Pd(bqd)_2$ (*1a*). However, the intra-stack Pt–Pt spacing was found to be shorter than the Pd–Pd separation of 3.202 Å. Moreover, the closely related $Pt(dmg)_2$ system (dmg^- = ion of dimethylglyoxime) crystallizing in the same orthorhombic space group Ibam, exhibits a Pt–Pt contact of 3.23 Å (*16*) which is much larger, despite the fact that the dmg ligand is substantially smaller than the bqd ligand. Although the Pt–Pt spacing in $Pt(bqd)_2$ is only 0.057 Å shorter than in $Pt(dmg)_2$, the electrical conductivity along the Pt chains is by a factor of at least 10^9 larger (*15, 17*). This abnormally large conductivity of $Pt(bqd)_2$ has been qualitatively attributed to the slight reduction in Pt–Pt distance which, in turn, was found to be the result of the reported ligand-induced nephelauxetic effect (*4, 5*). The effect, reminiscent of the phenomenon of through-bond coupling of lone pairs or π electron systems in organic molecules (*18, 19*), has been shown to dominate the overall electronic behavior, not only of these one-dimensional materials (*5*), but also of paramagnetic cluster compounds (*20*). To provide a reliable basis for an understanding of the solid state properties of $Pt(bqd)_2$, we have determined the full structure of this system by conventional X-ray techniques at ambient temperature as reported in the following.

Experimental Section

(a) Crystal Preparation

Prismatic crystals of $Pt(bqd)_2$ measuring about 8 × 0.4 × 0.2 mm were grown by the slow cooling of a saturated hot solution in "highest purity" 1,2-dichlorobenzene (99%+, Eastman Kodak) as reported.[1] The crystals gave an excellent microanalysis and were esr insensitive, thus demonstrating the absence of any noticeable paramagnetic impurities in the lattice. The near infrared spectrum suggests the presence of symmetric intramolecular O–H–O bridges, as the characteristic O–H stretching absorption band is virtually unobserved.

(b) Crystal Measurement and Diffraction Data

A black crystal with a metallic appearance measuring 0.35 × 0.25 × 0.15 mm was mounted on the tip of a thin glass fiber. Accurate determination of the unit cell based on the orientation matrix calculated from the exact centering of 15 reflections, and diffraction data collection were accomplished with a Syntex $P2_1$ four circle, computer controlled diffractometer using graphite-monochromated MoKα radiation under the experimental conditions reported previously (*21*). The unit cell crystallizes in the orthorhombic space group Ibam (D_{2h}^{26}), with the constants $a = 20.68(9)$Å, $b = 9.743(3)$Å, $c = 6.346(2)$Å, $V = 1279(1)$Å^3. It contains four formula units (with molecular weight = 469.33), in accord with the calculated density of $d_{calc} = 2.44$ g/cm^3 (compared to the observed value of $d_{obs} = 2.42$ g/cm^3, determined by floatation in CBr_4/CCl_3). Intensity measurements ($\theta/2\theta$ scans, $2\theta_{max} = 70°$) yielded 764 observed reflections, those with an intensity $I < 3.5\sigma(I)$ being classified as unobserved. Omega scans of five low angle reflections were recorded at a rate of two counts per second. Symmetric peaks were obtained with half-height widths ranging from 0.18 to 0.14°. The observed intensities were corrected with Lorentz and polarization factors,

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[1] The crystal used in this analysis was selected from the preparation of "Batch I" described in Ref. (*15*).

and were given statistical weights. Later, the 200 reflection (abnormally high difference between observed and calculated structure factor) and five weak reflections near the statistical cutoff were rejected. Thus, refinement was based on 758 structure factors.

(c) Determination and Refinement of the Structure

As shown by Weissenberg photographs, the Pt(bqd)$_2$ compound crystallizes isostructurally with the analogous α-Pd(bqd)$_2$ system described earlier (*1a*). Thus, the positions of nonhydrogen atoms of the Pd complex were inserted, the scale factor adjusted, and least-squares refinement was calculated first with isotropic, then with anisotropic temperature factors. Convergence was reached with an unweighted accuracy factor of $R = 0.052$ (weighted $R = 0.058$), a maximum shift/error of less than 0.01, and estimated standard deviation of an observation of unit weight equal to 1.549. Insertion and refinement of an extinction parameter gave no better result, nor did the insertion of hydrogen positions (peaks from a difference Fourier map near calculated hydrogen positions).

Calculations were carried out on a PDP 11/45 computer at Stanford (Department of Chemistry) using programs of the "Structure Determination Package" (*21*). Scattering factors were based on Vol. IV of the "International Tables for Crystallography" (*22*), anomalous terms were automatically inserted in structure factor calculations.

Description of the Structure

The lattice structure is homogeneous, that is it consists of neutral Pt(bqd)$_2$ complexes as the only "building stones." The molecular structure with bond distances and angles is represented by ORTEP plotting in Fig. 1. All the atoms lie in a mirror plane with $z = 0.0$ and with the Pt(II) core at the center of symmetry. Thus Pt(bqd)$_2$ is a completely *coplanar* centrosymmetric molecule. The four nitrogen atoms of the two bidentate ligands are coordinated to the central Pt in a rectangular arrangement, giving rise to the formation of two five-membered chelate rings. Symmetric O–H–O bridges (with an O–O separation of 2.653 Å), first inferred from near infrared spectroscopy (absence of the characteristic O–H stretching absorption band), then confirmed here by the equality (within experimental error) of the N–O bond distances and hence by the identical electron density around the oxygen atoms, produce two additional chelate

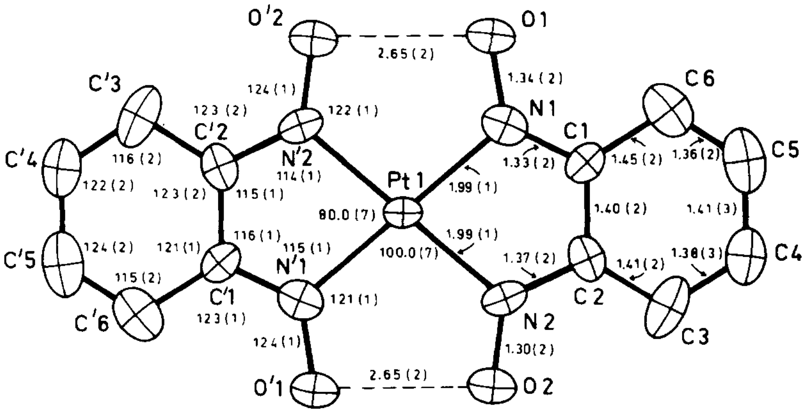


FIG. 1. ORTEP plot of the coplanar, centro-symmetric Pt(bqd)$_2$ molecule, showing bond distances (in Å) and angles (in degree) with their standard deviations given in parentheses.

rings. Positional and thermal parameters and their estimated standard deviations are listed in Table I.

In the crystal, the flat Pt(bqd)$_2$ units stack one on top of the other to form "infinite" molecular columns running parallel to one another throughout the lattice (Pt–Pt = 3.173 Å). Each molecular plane lies strictly perpendicular to the stacking direction (crystallographic *c* axis), and is rotated by an angle of 93° with respect to its nearest neighbors (Figs. 2, 3, 4). ORTEP projections of the orthorhombic cell onto the *ab* (0 0 0) and ($\frac{1}{2}$ 1 0) planes are shown in Figures 3 and 4, respectively. From Figure 2 one recognizes the existence of four slightly zigzagged chains of quaternized N atoms surrounding the Pt chain at a regular distance of 1.99 Å. Eight similar chains of alternating *C* and O atoms are also present, approximately 3.25 Å away from the central Pt chain. In Fig. 3, it is seen that there are two types of hose-like tunnels (I and II) running parallel between adjacent complex stacks and differing in their symmetry, size and chemical environment.

Discussion of the Structure

The most striking feature of the structure is the unusually short intrachain Pt–Pt contact of only 3.173 Å, which is the shortest observed so far in a Pt(II) derivative of this type. At first glance, this observation does not seem to be obviously understandable. It appears of primary concern, therefore, to try to establish, at least qualitatively, the nature and the origin of this important result. We note, to start with, the order of increasing radius of the divalent d^8-ions which is $\mathrm{Ni}^{2+} < \mathrm{Pd}^{2+} < \mathrm{Pt}^{2+}$. By virtue of the identical ligand field (*1*) surrounding these ions in the completely coplanar complexes of the analogous series Ni(bqd)$_2$, Pd(bqd)$_2$, Pt(bqd)$_2$, one would normally expect the van der Waals repulsion forces acting between the adjacent central metal ions, and hence the metal–metal contacts along the stacks, to increase in the same order. The observation of the opposite result is compatible with the reported ligand-induced nephelauxetic effect (*4–5*) which is expected to reduce the intrachain van der Waals repulsions between

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a,b,c]

Atom	*X*	*Y*	*Z*	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
Pt1	0.0000(0)	0.0000(0)	0.0000(0)	0.00131(1)	0.00566(5)	0.0155(1)	0.0014(2)	0.0000(0)	0.0000(0)
O1	0.1318(6)	0.902(1)	0.0000(0)	0.0021(3)	0.008(1)	0.028(4)	0.002(1)	0.0000(0)	0.0000(0)
O2	0.9606(6)	0.287(1)	0.0000(0)	0.0021(3)	0.008(1)	0.032(4)	0.003(1)	0.0000(0)	0.0000(0)
N1	0.0117(6)	0.203(1)	0.0000(0)	0.0022(5)	0.008(1)	0.015(3)	0.001(1)	0.0000(0)	0.0000(0)
N2	0.0961(5)	0.011(2)	0.0000(0)	0.0013(2)	0.009(1)	0.020(3)	0.002(1)	0.0000(0)	0.0000(0)
O1	0.0727(8)	0.245(2)	0.0000(0)	0.0013(3)	0.009(2)	0.021(4)	0.000(1)	0.0000(0)	0.0000(0)
O2	0.1200(8)	0.142(2)	0.0000(0)	0.0022(4)	0.007(1)	0.015(4)	−0.002(1)	0.0000(0)	0.0000(0)
O3	0.1868(9)	0.171(3)	0.0000(0)	0.0017(4)	0.020(4)	0.031(7)	−0.004(2)	0.0000(0)	0.0000(0)
O4	0.2032(10)	0.309(3)	0.0000(0)	0.0023(4)	0.013(2)	0.037(8)	−0.004(2)	0.0000(0)	0.0000(0)
O5	0.1556(13)	0.412(3)	0.0000(0)	0.0035(6)	0.013(3)	0.036(8)	−0.006(2)	0.0000(0)	0.0000(0)
O6	0.0910(11)	0.389(2)	0.0000(0)	0.0035(6)	0.009(2)	0.028(6)	−0.001(2)	0.0000(0)	0.0000(0)

[a] The form of the anisotropic thermal parameter is:

exp[−(B(1.1) * H * H + B(2.2) * K * K + B(3.3) * L * L + B(1.2) * H * K + B(1.3) * H * L + B(2.3) * K * L)].

[b] Standard deviations of the least significant digits are given in parentheses.

[c] The hydrogen positions were calculated and were not refined.

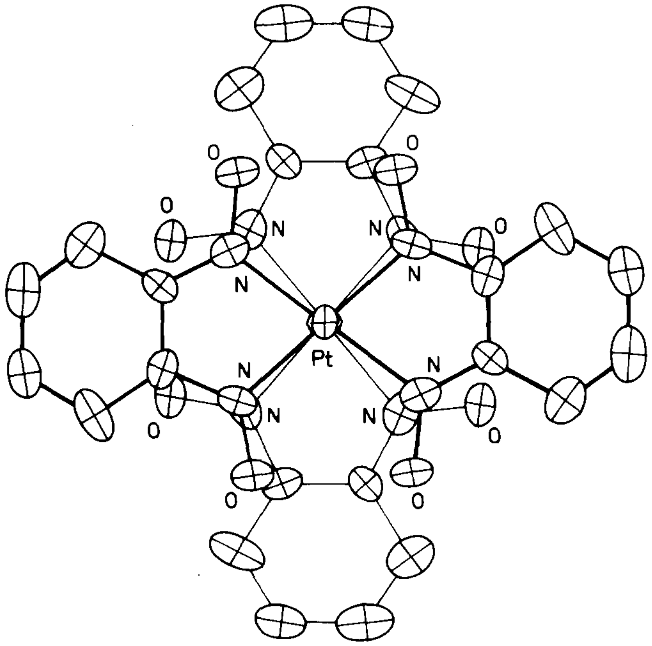


FIG. 2. ORTEP plot of a column of $Pt(bqd)_2$ molecules viewed down the Pt atom chain and showing the relative rotation of alternate complex units by an angle of 93°. The molecule drawn in light lines lies in the (0 0 0) plane underneath the nearest neighbor drawn in heavy lines and lying in the (0 0 $\frac{1}{2}$) plane. It is seen that the straight linear chain of Pt atoms is equidistantly surrounded by four slightly zig-zagged chains of quaternized N atoms (N–N ~ 3.18 Å). Eight similar chains are formed by alternate C–O contacts.

neighboring metal ions in the above order. Thus, the large metal–metal separations mentioned in the introduction for α-$Pd(bqd)_2$ and $Pt(dmg)_2$ compared to the short Pt–Pt contact observed here, ought to be most reasonably visualized in terms of the nephelauxetic effect which is much less in those compounds than in the present $Pt(bqd)_2$.

The metal-nitrogen (*M*–N) bond distance may be regarded as a reliable and meaningful estimate for the back bonding or "back donation" effect which interconnects the metal *d*-shell with the ligand mesomerism of π electrons. Considering a given metal core, *M*, in an $M(bqd)_2$ species, the contribution of "back donation" (*6*) to the *M*–N bond strength is obviously the larger, the higher the *d*-electron density at the metal site. One expects, therefore, the bond to be stronger, and hence shorter, at lower rather than at higher oxidation states of the central metal core. This appears to be conclusively demonstrated by the X-ray results displayed in Table II. Also, it has been observed that the near infrared stretching absorption of the C=N bond is sensitive to substitutions of the benzoquinonoid rings. When the substituents are electron withdrawing chromophores, the absorption is noticeably red-shifted (*4*). This is consistent with the expectation that reinforcement of the electrophilism of the benzoquinonoid ring ought to result in a withdrawal of some electron density from the electron rich C=N bond, thus reducing the oscillator strength of the bond. Conversely, electron releasing substituents shift the C=N absorption to higher frequency, as a result of the opposite effect. The nir results have thus provided a relevant argument to claim that electronic effects induced by appropriate substituents at the

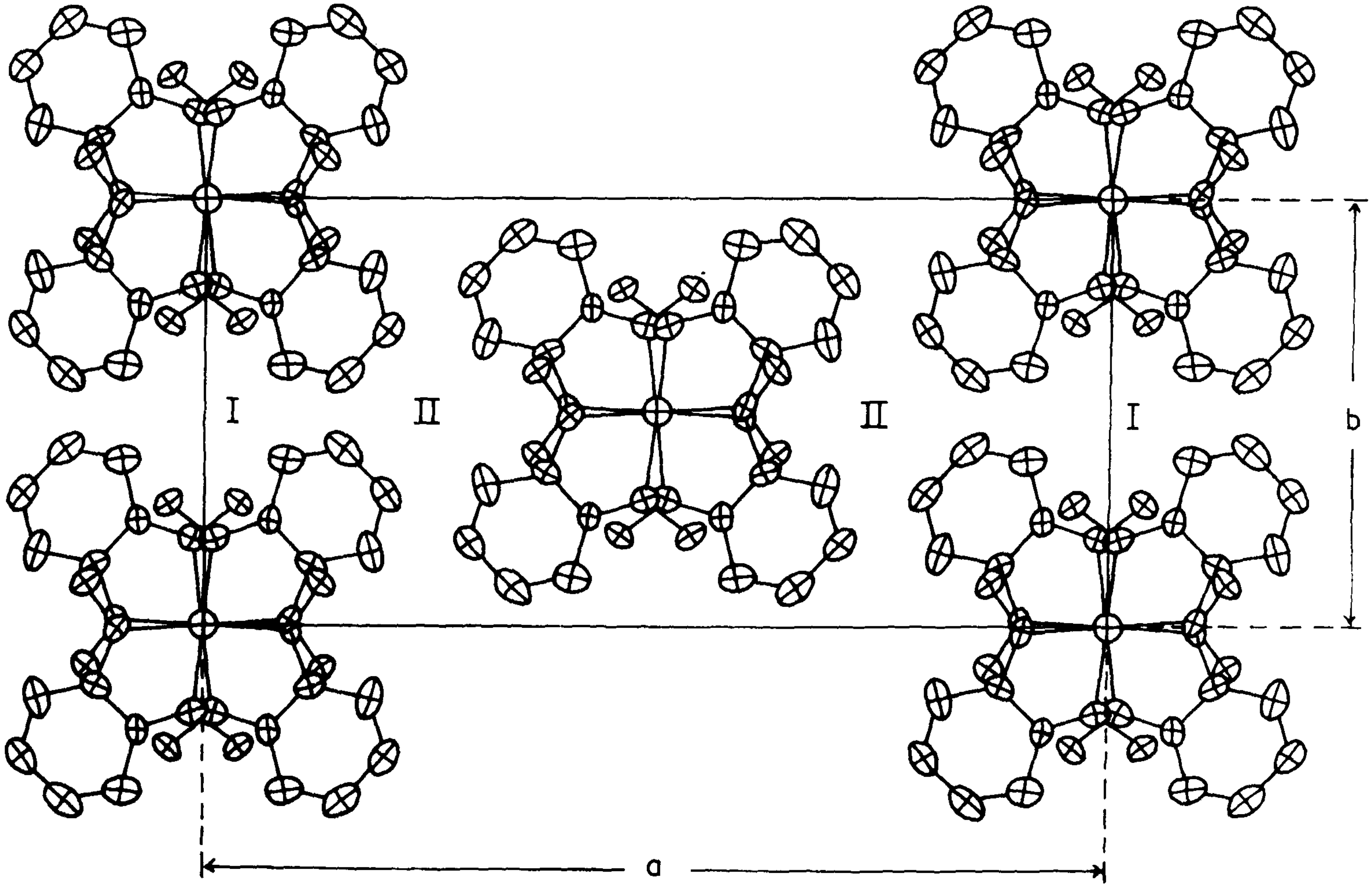


FIG. 3. Projection of the orthorhombic unit cell of $Pt(bqd)_2$ (ORTEP plot) onto the *ab* plane ($a = 20.68$ Å, $b = 9.743$ Å). Two types of hose-like tunnels (I and II) run parallel between adjacent molecular stacks. The tunnel types differ in shape, size and chemical environment.

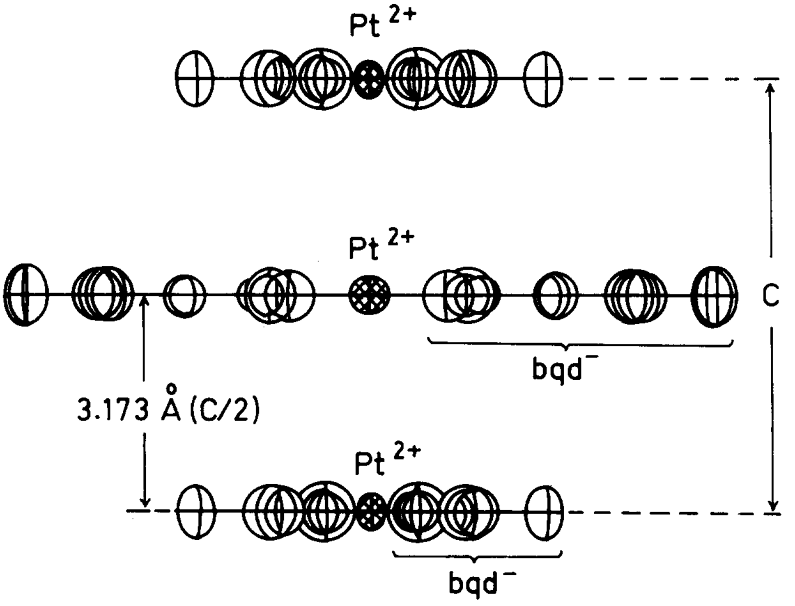


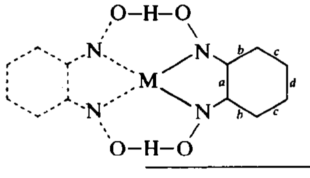
FIG. 4. ORTEP projection of the unit of Pt(bqd)$_2$ onto the ($\frac{1}{2}$ 1 0) plane, i.e., view perpendicular to the *c*-axis.

benzoquinonoid rings are mesomerically delocalized throughout the ligand system, and are transmitted to the N atoms, i.e., to the nearest vicinity of the central metal atom chain. This is a result of considerable significance, especially in connection with the high temperature excitonic superconductivity hypothesized by Little (*9*), for the feasibility of which the presence of highly polarizable dyelike side groups interacting directly with the central conduction spine is an indispensable prerequisite.

Finally, there appears to be a trend in the variation of the overall C–C bond distance, which indicates (particularly for bond *a* in Table II) that this distance is shortest

TABLE II

COMPARATIVE INTRAMOLECULAR BOND DISTANCES IN UNOXIDIZED AND OXIDIZED (*) M(bqd)$_2$ COMPLEXES



	Bond distance in Å							
Complex	M–N	C–N	N–O	*a*	*b*	*c*	*d*	Ref.
Ni(bqd)$_2$	1.864	1.310	1.32	1.445	1.43	1.35	1.43	*1b*
Ni(bqd)$_2$I$_{0.50}$*	1.905	1.31	1.33	1.50	1.43	1.37	1.42	*2*
α-Pd(bqd)$_2$	1.975	1.32	1.335	1.47	1.45	1.36	1.48	*1a*
Pd(bqd)$_2$I$_{0.55}$*	2.042							*4*
Pt(bqd)$_2$·(AgClO$_4$)$_{\frac{1}{2}}$	1.98	1.29	1.385	1.48	1.45	1.35	1.475	*3*
Pt(bqd)$_2$I$_2$*	2.002	1.32	1.33	1.46	1.43	1.365	1.445	*24*
Pt(bqd)$_2$	1.99	1.35	1.32	1.40	1.43	1.37	1.41	This work

within the organic part of Pt(bqd)$_2$ compared to other chelates of the same type (*1, 2, 16, 23*). The trend ought to be understood as a result of the nephelauxetic effect which is largest in Pt(bqd)$_2$ and is expected, therefore, to effect a substantial increase in formal electron density within the benzoquinonoid rings, so that the C–C bonds of this system may become strengthened and shortened noticeably.

Concluding Remarks

The overall crystal lattice of the linear metal–chain Pt(bqd)$_2$ is *isostructural* to that of the related compounds α-Pd(bqd)$_2$ (*1a*), Ni(dmg)$_2$ (*25*), Pd(dmg)$_2$ (*26*) and Pt(dmg)$_2$ (*16*), which crystallize in the common orthorhombic space group Ibam (D_{2h}^{26}). The most salient distinction of scientific significance between these lattice structures, however, relates to their differing intrachain metal–metal contact which is shortest in Pt(bqd)$_2$, as a result of the larger ligand-induced nephelauxetic effect (*4, 15*).

[2] Auxiliary Material: A listing of observed and calculated structure factor amplitudes, F_{hkl} (4 pages), has been deposited with the National Auxiliary Publications Service (NAPS), and will appear in Microfiche Publications. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017.

Acknowledgments

The author is grateful to Professor W. A. Little for his stimulating interest. I am indebted to Dr. H. Endres for his invaluable help with the refinement of the structure. The very kind help of Professor K. O. Hodgson, Dr. M. A. Bobrik and J. M. Berg on the structure determination is gratefully acknowledged.

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