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The Structure of Binary Metal Dimethylglyoximates Containing Nickel, Palladium, or Platinum

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Binary metal dimethylglyoximates containing nickel and palladium, nickel and platinum, or palladium and platinum have been prepared and their unit-cell dimensions have been obtained by X-ray diffraction. These binary complexes are isomorphous with the simple dimethylglyoximates of nickel, palladium, and platinum and have metal-metal distances within the range 3.23 — 3.25 ± 0.02 Å.

Introduction

Godycki and Rundle[1] have determined the crystal structure of bis(dimethylglyoximato)nickel(II) and have shown that the square-planar molecules are stacked one above the other so that the nickel atoms lie in chains which extend throughout the crystal. Bis(dimethylglyoximato)palladium(II)[2] and bis(dimethylglyoximato) platinum(II)[3] have been shown to be isomorphous with the nickel compound. The close approach (~ 3.25 Å) of adjacent metal atoms in these structures has been rationalized in terms of metal-metal bonding and several workers have attempted to investigate the nature of these bonds.[4-10] However, it has been suggested that metal-metal bonds may not be present in these compounds and the unusual structure of these complexes may in fact be mainly due to fâvourable crystal packing.[11-14]

Basu *et al.*[14] prepared a series of binary mixed products containing nickel, palladium, platinum, or copper dimethylglyoximates by crystallizing the individual compounds, in the required ratio, from chloroform solutions but the crystalline products were not characterized by elemental analysis. These authors investigated the visible spectra of the binary products and found that some had peaks characteristic of both components of the mixture, whereas others had peaks which were not clearly defined. However, all the spectra were interpreted as containing bands belonging to each component in the crystal. It was postulated that the position of the bands in some cases altered due to incidental environmental factors. From these results it was concluded that the transitions observed were of a localized moleculra variety as opposed to non-localized transitions involving a chain of metal atoms.

Banks and Barnum[8] have determined the spectra of colloidal suspensions of mixed crystals of nickel, palladium, and platinum complexes of 4-methylnioxime. They found that each spectrum consisted of a single peak which lay between the two peaks in the spectrum of a mechanical mixture of the two components. In contrast to the conclusion drawn for the dimethylglyoxime complexes,[14] this result suggests that the transitions in these mixed crystals are of the non-localized type involving metal atom chains.

Results and Discussion

Binary metal dimethylglyoximates containing nickel, palladium, or platinum have been prepared. Crystallization from dimethylformamide rather than from chloroform was found to be more satisfactory. The compositions of these binary metal complexes have been determined by elemental analysis and their structures have been investigated by X-ray diffraction. When the ratio of the dissolved complexes was 1: 1, the crystals which were isolated also contained the component complexes in ratios which approximated to 1: 1. Recrystallization did not significantly alter these ratios even though the solubilities of the individual nickel, palladium, and platinum complexes in dimethylformamide are considerably different. All the mixed metal products are diamagnetic.

The solid state reflectance spectrum of a ground sample of the nickel-palladium compound in the range 400-600 mμ is considerably different from that of a ground 1: 1 mixture of the separate nickel and palladium complexes (see Fig. 1). The positions of the bands in each spectrum are quite close to the positions observed by Basu *et al.*[14] for similar samples whose transmission spectra were determined on sodium chloride pellets.

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The infrared spectra of the nickel, palladium, and platinum dimethylglyoxime complexes have been investigated by other workers[15-18] and most of the bands have been assigned; however, these assignments in many cases are complicated by the very weak, broad nature of the bands.[17,19] The spectra of the mixed-metal complexes reported here have also been obtained and have been compared with those of the individual complexes and with mechanical mixtures of these complexes. The overall pattern of the spectra of the 1:1 complexes is very similar to that of the corresponding ground mixtures; however, certain bands, in particular ν_{OH} ($\sim$ 2350 cm^{-1}) and δ_{OH} ($\sim$ 1750 cm^{-1}), are ill-defined in the spectra of both the binary complexes and the mechanical mixtures.

Single crystals of $(Ni,Pd)(DMG)_2$ (see preparation No. 2, Experimental section) grow as orange needles elongated in a direction perpendicular to (001). They are orthorhombic with the unit-cell dimensions listed in Table I.

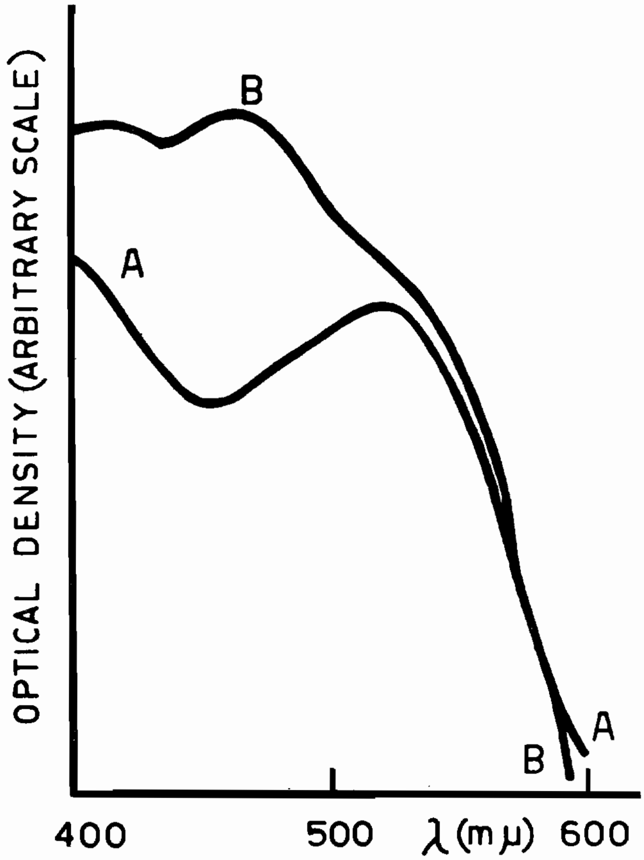

Figure 1. Reflectance spectra: A. $(Ni,Pd)(DMG)_2$; B. 1:1 Mechanical mixture of $Ni(DMG)_2$ and $Pd(DMG)_2$.

Systematic absences determine the space group as *Ibam* or *Iba*. The substance is obviously isomorphous with $Ni(DMG)_2$, $Pd(DMG)_2$, and $Pt(DMG)_2$ and the very weak intensities of the *hkl* data with $l \neq 2n$ is in keeping with the transition metal atoms occupying positions 4(c) of the space group *Ibam*, *i.e.* in the mirror planes, $z = 0$ and $z = 1/2$. The intriguing feature which now emerges is that the two nickel and two palladium atoms in the unit cell occupy four *equivalent* crystallographic positions. There are two possible explanations of this phenomenon. The first is that the 'single' crystal consists of domains of $Ni(DMG)_2$ and $Pd(DMG)_2$ which intergrow and in effect produce a mixed crystal. Transmission microscopy failed to provide any evidence to support this. The alternative, and more likely explanation, is that $Ni(DMG)_2$ and $Pd(DMG)_2$ molecules stack on top of each other, in the manner found in simple dimethylglyoximates of these metals but that stacking disorder occurs in each infinite chain of molecules. Instead of a regular alternation of palladium and nickel atoms, there is an occasional Ni-Ni interaction or Pd-Pd interaction which results in the situation depicted in Fig. 2. Thus in any unit-cell in the crystal the probability of finding a palladium atom at one of the crystallographic positions 4(c) of space group *Ibam* is the same as that of finding a nickel atom, and the 'average' or statistical atoms thus found are crystallographically equivalent.

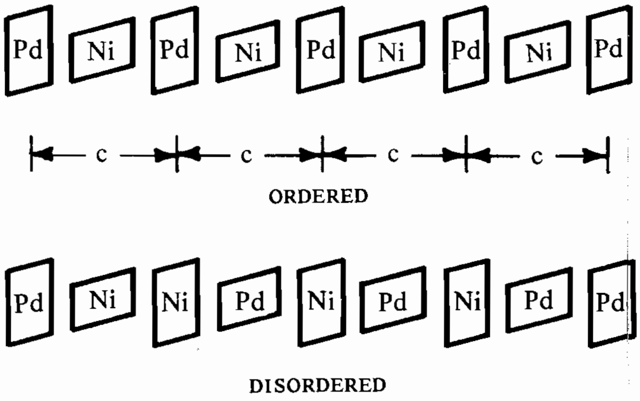

Figure 2.

An attempt was made to change the nature of the 'average atom' by increasing the ratio of nickel to palladium atoms on the chain. Single crystals were grown from a solution in which the molar ratio of $Ni(DMG)_2$ to $Pd(DMG)_2$ was 3:1 (preparation No. 4, Experimental). Analysis showed that these crystals differed significantly from the previous ones and that the ratio of nickel to palladium atoms, although not exactly 3:1, was significantly greater than 1:1. However, these crystals were again isomorphous with the 1:1 crystals and stacking disorder occurs in each infinite chain of molecules due to the probability of Ni-Ni and Pd-Pd interactions as well as Ni-Pd interactions.

Were the stacking sequence of metal atoms in each infinite molecular chain to be always Ni-Pd-Ni- *etc.*, with no stacking faults, then the mixed metal complexes would *not* be isomorphous with the simple metal

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dimethylglyoximates: they might have similar cell dimensions but would not have the same space group because of the ordering of the metal atoms. An attempt to grow such crystals was made by allowing a 1:1 solution of $Ni(DMG)_2$ and $Pd(DMG)_2$ to cool very slowly from 150°C to room temperature over a period of three days (preparation No. 3, Experimental). Beautiful crystals were obtained but these gave identical photographs with those from the disordered crystals.

Mixed nickel-platinum and palladium-platinum dimethylglyoximates were also prepared. The single crystals are isomorphous with the simple metal dimethylglyoximates. The unit-cell dimensions are listed in Table 1. The metal-metal distances in the binary metal complexes are the same, within experimental error, as in the simple metal dimethylglyoximates.

Table I. Crystallographic Data on Dimethylglyoxime Complexes

Cell dimensions	$Ni(DMG)_2$[20]	$Pd(DMG)_2$[2]	$Pt(DMG)_2$[3]
a	16.68 Å	16.73 Å	16.73 Å
b	10.44	10.47	10.59
c	6.49	6.51	6.47
M-M distance	3.25	3.26	3.24
	$(Ni,Pd)(DMG)_2$	$(Ni,Pt)(DMG)_2$	$(Pt,Pd)(DMG)_2$
a	16.64 ± 0.08 Å	16.74 ± 0.08 Å	16.80 ± 0.08 Å
b	10.43 ± 0.05	10.44 ± 0.05	10.54 ± 0.05
c	6.46 ± 0.03	6.45 ± 0.03	6.49 ± 0.03
M-M distance	3.23 ± 0.02	3.23 ± 0.02	3.25 ± 0.02

Conclusion

The X-ray data show that the binary products are not mixed crystals consisting of domains of the individual metal dimethylglyoximates but are homogeneous in that a cell can be chosen representative of the whole single crystal in which both metal dimethylglyoximate molecules are stacked in a statistically ordered manner. The visible spectra are in agreement and the infrared data, although indefinite, are not at variance with the structure found by the X-ray investigation.

Experimental Section

The bis(dimethylglyoximato)nickel, palladium, and platinum complexes were prepared by published methods.

Preparation of Binary Metal Complexes. Stoichiometric amounts (1:1 unless otherwise stated) of the component complexes were dissolved in a minimum amount of hot dimethylformamide (DMF). The solution was then brought to the boil, quickly filtered, and allowed to cool as described below. All products were dried at 115°.

Nickel-Palladium Dimethylglyoximate. 1. The solution was allowed to cool for 20 min. to yield orange needles (Found: C, 30.6; H, 4.35; N, 17.7; Ni, 9.0; Pd, 17.7. The 1:1 complex, $C_{16}H_{28}N_8NiO_8Pd$ requires C, 30.7; H, 4.5; N, 17.9; Ni, 9.4; Pd, 17.0%).

2. Some of the above product was recrystallized from boiling DMF. The solution was allowed to cool quickly to room temperature (Found: C, 30.45; H, 4.6%).

3. Some of the product from prepn. 1 was recrystallized from boiling DMF and the solution was allowed to cool over 3 days in a dewar flask (Found : C, 31.0; H, 4.7%).

4. The component complexes were mixed in the ratio (Ni:Pd = 3:1) and the boiling solution was allowed to cool to 80°. The orange-red crystals were filtered off, recrystallized from boiling DMF, and allowed to cool over 3 days (in dewar) (Found: C, 32.5; H, 4.8. The 3:1 complex $C_{32}H_{56}N_{16}Ni_3O_{16}Pd$ requires C, 32.0; H, 4.7%).

Nickel-Platinum Dimethylglyoximate. 5. The solution containing the component complexes was cooled and the lustrous dark brown needles that formed were isolated and recrystallized from boiling DMF. The solution was let cool over 3 days (in dewar) (Found: C, 27.5; H, 3.7; N, 16.2. The 1:1 complex $C_{16}H_{28}N_8NiO_8Pt$ requires C, 26.9; H, 4.0; N, 15.7%).

6. The solution containing the component complexes in the ratio (Ni: Pt = 2:1) was allowed to cool to 80° and the dark brown product was filtered off and recrystallized from boiling DMF. The solution was let cool over 3 days (in dewar) (Found: C, 28.9; H, 4.3. The 2:1 complex $C_{24}H_{42}N_{12}Ni_2O_{12}Pt$ requires C, 28.8; H, 4.2%).

Palladium-Platinum Dimethylglyoximate. 7. The solution was allowed to cool quickly and the brown needles were isolated (Found: C, 25.6; H, 3.7; Pd + Pt, 39.8. The 1:1 complex $C_{16}H_{28}N_8O_8PdPt$ requires C, 25.2; H, 3.7; N, 14.7; Pd + Pt, 39.6%).

8. Preparation 7 was repeated except that the solution was cooled over 3 days (in dewar). (Found : C, 25.6; H, 3.7; N, 15.2%).

9. The component complexes were mixed in the ratio (Pd : Pt = 2 : 1) and the boiling solution was allowed to cool to 80°. The brown needles were recrystallized from DMF and the solution was allowed

to cool slowly (Found: C, 27.1; H, 3.9. The 2 : 1 complex $C_{24}H_{42}N_{12}O_{12}Pd_2Pt$ requires C, 26.3; H, 3.9%). The analytical figures show that the composition of the product does not correspond exactly to the 2: 1 complex.

X-ray Data. The X-ray data were collected using equi-inclination Weissenberg geometry with CuK_α radiation. Zero level precession photographs were also used (MoK_α radiation) and these photographs gave information leading to the unit-cell dimensions listed in Table 1. These dimensions are considered accurate to 0.5%. The systematic absences in X-ray data are hkl with $h+k+l \neq 2n$, $0kl$ with $k \neq 2n$ and $h0l$ with $h = 2n$.

Spectra. The reflectance spectra were measured on a Zeiss PMQ II spectrophotometer. The samples were prepared by grinding and were spread uniformly on filter papers.

The infrared spectra were obtained from Nujol and halocarbon mulls. The measurements were made on a Perkin-Elmer 337 spectrophotometer.

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