ride, 0.7610 g. (0.00663 mole) of indium and 0.1792 g. (0.00664 mole) of aluminum were employed, the reaction temperature being 325°.

For analysis, the product was dissolved in nitric acid, hydrogen chloride evolved being trapped and combined with the solution. The separation of indium was effected by the method of Moser and Siegmann,[19] in which indium was precipitated as the sulfide while the aluminum was kept in solution by means of sulfosalicylic acid in an ammonium acetate–acetic acid buffer. The sulfide was dissolved with dilute hydrochloric acid and the indium found as described previously. The aluminum was determined on an aliquot of the indium-free solution by precipitation with 8-hydroxyquinoline.[20] Another aliquot was analyzed for chloride as described for the indium chlorides. *Anal.* Calcd. for $InAlCl_4$: In, 40.47; Al, 9.51; Cl, 50.02. Found: In, 40.51; Al, 9.69; Cl, 49.74.

Discussion

The color of $InAlCl_4$ generally was white in the solid state but occasionally showed a yellow appearance. It melted sharply at 267–268° to give a colorless or pale yellow melt and was extremely sensitive to moisture. Its identity as a true compound was demonstrated by a study of melting behavior in the system $InCl$–$AlCl_3$ (Fig. 2). The technique employed in this study was that described for the $InCl$–$InCl_3$ system. It is apparent from Fig. 2 that a sharp maximum occurs at 50 mole % InCl. Moreover, the melting point and appearance of the material at this composition were identical with those of $InAlCl_4$ prepared by the procedure noted above. In view of the ability of aluminum chloride to function as a Lewis acid, there is little doubt that the compound should be formulated as indium(I) tetrachloroaluminate, $In[AlCl_4]$.

Indium(I) tetrachloroaluminate exhibits interesting behavior toward ether. Even when exposed to ether vapor, the compound immediately turned brilliant yellow. Treatment with an excess of liquid ether left a yellow residue which upon analysis proved to be indium monochloride.[21] The ether solution was found to contain no indium but contained aluminum chloride. Here again, as in the ether extractions of In_2Cl_3, it seems reasonable to suppose that the ether, functioning as a stronger Lewis base than chloride ion, replaces the latter from combination with aluminum chloride.

$$In[AlCl_4] + Et_2O \longrightarrow InCl + AlCl_3{\cdot}Et_2O$$

Acknowledgments.—The authors are indebted to the Atomic Energy Commission for a grant in support of this investigation. R. J. C. wishes to express his appreciation to the Eastman Kodak Company for a fellowship held during part of the investigation.

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[19] L. Moser and F. Siegemann, *Monatsh. Chem.*, **55**, 14 (1930).

[20] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 507.

[21] Since the monochloride as made by high temperature procedures is deep red in color, it is conceivable that the yellow form is a different crystalline modification.

LAWRENCE, KANSAS

[CONTRIBUTION NO. 619 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Intermolecular Metal–Metal Bonds and Absorption Spectra of Some Nickel(II) and Palladium(II) Complexes of *vic*-Dioximes[1]

BY CHARLES V. BANKS AND DENNIS W. BARNUM

RECEIVED MARCH 15, 1958

Intermolecular metal–metal bonds in certain square planar complexes of Ni(II), Pd(II), Pt(II) and Au(III) give rise to an absorption band in the visible region of the spectrum. This band gives rise to unusual dichroism in crystals of these complexes. The absorption spectra of single crystals of some nickel complexes were measured using plane polarized light and it was shown that complexes containing strong metal–metal bonds show "abnormal" dichroism while complexes with very weak metal–metal bonds show practically "normal" dichroism. The absorption spectra of colloidal suspensions of several of the complexes were measured. The position of the band due to metal–metal bonding depends primarily on the length of the metal–metal bonds, the central metal ion and the crystal structure. The position of this band also depends, but to a much lesser extent, on the particle size, since this affects the selective scattering of light on the long wave length side of an absorption band.

Introduction

Certain square planar complexes of nickel(II), palladium(II), platinum(II) and gold(III) have been shown to contain intermolecular metal–metal bonds.[2–4] These bonds form a chain of metal atoms that extends throughout the length of the crystal. The lengths of these relatively weak metal–metal bonds range from about 3.2 to 3.6 Å. Nevertheless, they contribute enough to the stability of the crystal that they affect the properties appreciably. The most striking example of this is the outstanding selectivity of nickel dimethylglyoxime as a gravimetric reagent for nickel.[2] The solubility of several complexes containing metal–metal bonds is discussed in the preceding paper.[5]

Complexes containing metal chains have an absorption band in the visible region of the spectrum. This band is most easily detected in the absorption spectrum of the complex in colloidal suspension and it gives rise to unusual dichroism in the single crystal.

Yamada and Tsuchida,[6] using plane polarized light, measured the absorption spectra of microscopic crystals of the copper(II), nickel(II) and

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[1] No. XXII in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XXI, THIS JOURNAL, **80**, 3579 (1958). Abstracted from dissertation submitted by Dennis W. Barnum to graduate faculty of Iowa State College in partial fulfillment of requirements for degree of doctor of philosophy, 1957.

[2] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[3] R. E. Rundle, THIS JOURNAL, **76**, 3101 (1954).

[4] M. Atoji, J. W. Richardson and R. E. Rundle, *ibid.*, **79**, 3017 (1957).

[5] C. V. Banks and D. W. Barnum, *ibid.*, **80**, 3579 (1958).

[6] S. Yamada and R. Tsuchida, *ibid.*, **75**, 6351 (1953).

platinum(II) complexes of dimethylglyoxime. Although copper dimethylglyoxime has almost identically the same molecular structure as nickel dimethylglyoxime,[7] it crystallizes with an entirely different structure in which chains of –Cu–Cu– bonds are not possible. For the nickel(II) and platinum(II) complexes it was found that maximum absorption of visible light occurs when the electric vector of the polarized light is perpendicular to the plane of the molecules, while for copper dimethylglyoxime and other "normal" square planar complexes maximum absorption occurs when it is parallel to the plane of the molecules. Yamada and Tsuchida[6] attributed this to an interaction between adjacent nickel atoms and between adjacent platinum atoms.

In the same manner, Yamada[8] showed that there is an interaction between adjacent platinum(II) atoms in the Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$. Atoji, Richardson and Rundle[4] have since shown that the green isomer contains intermolecular –Pt–Pt– bonds while the pink isomer does not. The pink color is characteristic of the $Pt(NH_3)_4^{++}$ ion and the green color is due to the platinum chains.

Colloidal suspensions of nickel dimethylglyoxime and of bis-(1,2-cyclohexanedionedioximato-N,N′)-nickel(II), *i.e.*, nickel nioxime, previously have been used by Juza and Langheim[9] and by Ferguson and Banks[10] in the spectrophotometric determination of nickel. In this work it is shown that this band is due to the metal–metal bonds.

Experimental

Crystal Structure.—As described in the previous paper[5] all of the complexes studied, except bis-(1,2-cycloheptanedionedioximato-N,N′)-palladium(II), *i.e.*, palladium heptoxime, and possibly nickel 4-*t*-amylnioxime, have crystal structures similar to that of nickel dimethylglyoxime.

Measurement of Metal–Metal Bond Lengths.—The methods used to measure the metal–metal bond lengths are described in the preceding paper.[5]

Preparation of Colloidal Suspensions.—Colloidal suspensions were prepared simply by precipitating the nickel or palladium complex in the presence of a protective colloid such as gum arabic or gelatin at the proper *p*H. The resulting suspension is stable for several weeks.

A known amount of nickel(II) perchlorate or of palladium(II) perchlorate was added to a 100-ml. volumetric flask and either 10 ml. of 10% gum arabic solution or 10 ml. of 1% gelatin solution was added. The *vic*-dioxime was then added in about 50% excess, followed by the addition of two drops of 2 *M* ammonium hydroxide. Water was added until the volume was about 99 ml. and the mixture allowed to stand for 1 hr. at room temperature. This mixture was then diluted to 100 ml. and the absorption spectrum determined with a Cary, Model 14, recording spectrophotometer. The spectra of the metal complexes were measured using a 10.0-cm. light path through the suspensions. The absorption spectra were found to be the same whether gelatin or gum arabic was used as the protective colloid. α-Benzildioxime is so insoluble in water that it was necessary to add this reagent as a hot saturated solution.

Colloidal suspensions of mixed crystals were prepared in a similar manner. The metals were mixed in solution and then gum arabic and the *vic*-dioxime were added in that order.

The non-aqueous suspensions were prepared by dissolving the *vic*-dioxime in the particular solvent to be used and then adding a saturated solution of anhydrous nickel chloride in the same solvent with vigorous stirring. Each spectrum was measured immediately after mixing.

Measurement of Absorption Spectra in Chloroform.—Solutions of known concentration were prepared by weighing the solid complex accurately on a microbalance and transferring the complex to a 100-ml. volumetric flask with chloroform. About 60 ml. of solvent then was added and the complex dissolved with the aid of heat. After dissolution was complete, the flask was filled to about 99 ml. and allowed to cool. Final dilution to exactly 100 ml. was not made until just before the absorption measurements were made. The solutions were transferred to glass-stoppered cells as quickly as possible, taking care to keep loss of solvent by evaporation to a minimum.

Spectra were scanned on an automatic recording Cary, Model 14, spectrophotometer. For the measurement of molar absorptivities of bands, a Beckman, Model DU, spectrophotometer with photomultiplier-attachment was used. Cooling water was circulated through the lamp housing to prevent heating in the cell compartment.

The chloroform was reagent grade quality.

Measurement of Absorption Spectra of Single Crystals.—The crystals available were so small that it was necessary to use the method of Tsuchida and Kobayashi[11] to measure their absorption spectra. In this method a polarizing microscope, mounted horizontally, is used to project an image of the crystal on the slit of a spectrograph. The spectrum is recorded photographically.

Results and Discussion

Absorption Spectra of Colloidal Suspensions.—In Fig. 1 the absorption spectrum of bis-(1,2-cycloheptanedionedioximato-N,N′)-nickel(II), *i.e.*, nickel heptoxime, in colloidal suspension is compared with its spectrum in chloroform solution. It is obvious that the suspension has a band that is not present in the spectrum of the solution. The same comparison was made with a number of other nickel and palladium complexes, known from X-ray measurements to contain metal–metal bonds, and in each case it was found that the spectrum of the solid contained a new absorption band. Because the difference in electronic structure between the molecules in solution and in the crystal is due to the metal–metal bonds, these must be responsible for the new absorption band. Rundle[12,13] has suggested that these bands are due to the transition of electrons from the band constituting the metal–metal bonds to the b_{1g}^* molecular orbital.

The absorption spectra of the dry solid complexes pressed into KBr discs also were measured and these were found to be almost identical with those of the colloidal suspension. The exact position of the metal–metal absorption band varied no more than 4 mμ from its position in the suspension.

Yamasaki and Matsumoto[14] have attributed this visible absorption band to the hydrogen bonds. However, hydrogen bonds are present both in the solid state and in the dissolved state, and one would not expect an appreciable change in absorption without some change in the electronic structure of the molecule.

The absorption spectra of chloroform solutions of nickel(II) and palladium(II) complexes of *vic*-dioximes that do not contain aromatic substituents

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(7) S. Bezzi, E. Bua and G. Schiavinato, *Gazz. chim. ital.*, **81**, 856 (1951).

(8) S. Yamada, THIS JOURNAL, **73**, 1579 (1951).

(9) R. Juza and R. Langheim, *Angew. Chem.*, **50**, 255 (1937).

(10) R. C. Ferguson and C. V. Banks, *Anal. Chem.*, **23**, 1486 (1951).

(11) R. Tsuchida and M. Kobayashi, *Bull. Chem. Soc. Japan*, **13**, 619 (1938).

(12) R. E. Rundle, private communication.

(13) R. E. Rundle, *J. Chem. Phys.*, **61**, 45 (1957).

(14) K. Yamasaki and C. Matsumoto, *Sci. Repts.* (*Osaka Univ.*), **No. 2**, 35 (1953).

are practically identical. Thus, the spectra of nickel dimethylglyoxime, nickel nioxime, nickel 4-methylnioxime, etc., are all very similar to that of nickel heptoxime shown in Fig. 1 (compare $\lambda_{\max}$ and $\epsilon_{\max}$ values in Table I), while the spectra of nickel α-furildioxime and nickel α-benzildioxime in chloroform show additional maxima at 435 mμ and at 406 mμ, respectively. These additional maxima are probably due to conjugation of the *vic*-dioxime with the aromatic groups. The same situation is true for the palladium complexes.

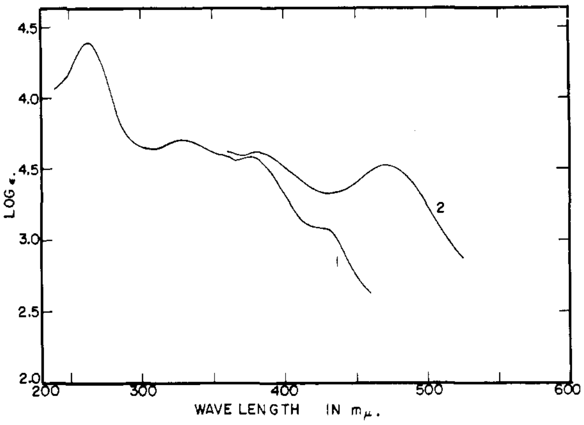

Fig. 1.—Absorption spectra of nickel heptoxime: 1, chloroform solution; 2, colloidal suspension.

However, in the colloidal suspensions of these complexes, the spectra are all different. In the nickel complexes the absorption band due to the metal–metal bonds varies from 465 to 557 mμ and in the palladium complexes it ranges from 425 to 482 mμ.

In most cases the position of the absorption band due to the metal–metal bonding is obvious. However, in nickel α-furildioxime this band is partially obscured by a nearby, more intense band, and in palladium α-furildioxime it is totally obscured. The position of the band was estimated in each case by resolving the total spectrum into its component bands. This was done by means of the equation for an absorption band given by Jørgensen[15]

$$\log \epsilon_0 = \log \epsilon + \left[\frac{\lambda - \lambda_0}{\beta}\right]^2 \qquad (1)$$

In this equation λ_0 and ϵ_0 are the wave length and molar absorptivity of the band at the point of maximum absorption, and β is a parameter which determines the half width of the band. The value of β may be different for the long wave length and the short wave length side of a band, in which case it is designated as β_+ or β_-, respectively. Values of λ_0, ϵ_0 and β are varied empirically until the sum of the individual bands gives the total observed absorption within reasonable limits.

In the case of nickel α-furildioxime the two bands which were obtained have the following parameters: λ_0 482 mμ, ϵ_0 9950 and β = 49 for one band, and λ_0 537 mμ, ϵ_0 3650 and β = 40 for the band due to nickel–nickel bonds. For both of these bands $\beta_+ = \beta_-$.

The absorption spectrum of palladium α-furildioxime also was resolved into its component bands. In this case it was necessary to postulate three bands in order to obtain the observed spectrum. The parameters of the three bands are: λ_0 387 mμ, ϵ_0 9950, β = 43; λ_0 422 mμ, ϵ_0 8800, β_+ = 42, β_- = 39; λ_0 460 mμ, ϵ_0 3250 and β = 42. The band at 460 mμ is believed to be due to palladium–palladium bonding.

It should be emphasized that the component bands are contrived to fit the experimental data and one should not put too much stock in the results. In the case of nickel α-furildioxime the shoulder on the long wave length side of the 475 mμ band in the colloidal suspension definitely indicates the presence of a band in the region of 540 mμ. For palladium α-furildioxime, however, the total absorption does not indicate such a band, and the resolution is more uncertain. The fact that the 460 mμ band in palladium α-furildioxime agrees closely with the 537 mμ band in the nickel complex, both in intensity and in band width, lends support for the results that were obtained.

It can be seen in Table I that there is a correlation between the position of the band due to metal–metal bonding and the length of the metal–metal bonds. In Fig. 2 these data are plotted for the nickel complexes and for the palladium complexes. The fact that nickel α-furildioxime and palladium α-furildioxime fall on their respective curves is additional support for the validity of the resolution of the total absorption into its component bands.

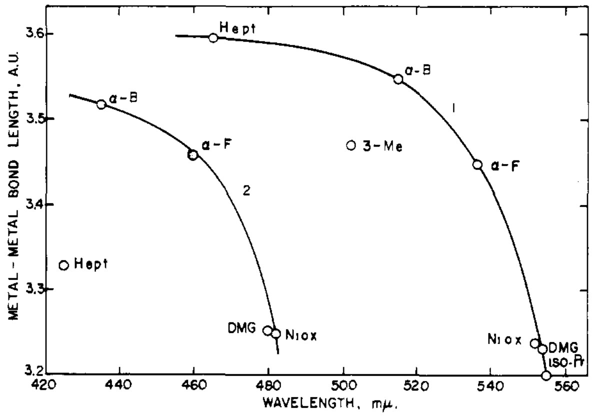

Fig. 2.—Dependence of the absorption band due to metal–metal bonding on the length of the metal–metal bonds: curve 1, nickel *vic*-dioxime complexes; curve 2, palladium *vic*-dioxime complexes.

Palladium heptoxime, which has a slightly different crystal structure than the other complexes, does not fall on the curve with the other palladium complexes although the crystal contains –Pd–Pd– bonds. Thus, it appears that the crystal structure is a factor affecting the position of this band. Also, nickel 3-methylnioxime does not fall on the curve. No explanation can be offered for this discrepancy.

The direction of this effect can be explained on the basis of the extent of delocalization of the electrons constituting the metal–metal bonds. It has long been known that in conjugated organic systems the absorption band moves steadily toward longer wave lengths as the π-electrons in such sys-

(15) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

TABLE I

METAL–METAL BOND LENGTHS AND ABSORPTION PROPERTIES OF METAL(II)-*vic*-DIOXIME COMPLEXES

Complex	–M–M– bond length, Å.	Solid complex λ_{max} of –M–M– band, mμ	Color	Chloroform soln. λ_{max}, mμ	Chloroform soln. ϵ_{max}, l./mole-cm.
Nickel dimethylglyoxime	3.233	554	Brick-red	262	2.45×10^4
				327	4.58×10^3
				374	3.43×10^3
Nickel nioxime	3.237	552	Scarlet	265	2.35×10^4
				333	5.02×10^3
				383	3.57×10^3
Nickel α-furildioxime	3.448	537	Red	293	3.90×10^4
				384	1.04×10^4
				435	1.52×10^4
Nickel α-benzildioxime	3.547	515	Orange	273	4.03×10^4
				361	9.89×10^3
				406	1.09×10^4
Nickel heptoxime	3.596	465	Yellow	263	2.49×10^4
				330	5.05×10^3
				377	4.05×10^3
Nickel 4-*t*-amylnioxime	3.2	547	Scarlet		
Nickel 4-isopropylnioxime	3.19	557	Scarlet		
Nickel 4-methylnioxime	3.24	547	Scarlet		
Nickel 3-methylnioxime	3.47	503	Orange		
Palladium nioxime	3.250	482	Yellow	242	2.74×10^4
				274	1.39×10^4
				383	1.95×10^3
Palladium dimethylglyoxime	3.253	480	Yellow	242	2.22×10^4
				275	1.26×10^4
				374	1.81×10^3
Palladium α-furildioxime	3.459	460	Orange	252	2.47×10^4
				285	4.11×10^4
				379	2.00×10^4
Palladium α-benzildioxime	3.517	435	Yellow	245	3.27×10^4
				267	3.56×10^4
				324	1.96×10^4
Palladium heptoxime	3.329	425	Yellow	243	2.13×10^4
				278	1.37×10^4
				370	1.87×10^3

tems become more delocalized. It is believed that a similar situation exists in the metal chains. Delocalization is greatest in those complexes with the shortest metal–metal bonds and the absorption band is found at longer wave lengths. As the metal–metal bond length increases the electrons become more localized on a particular metal atom and the band shifts to shorter wave lengths.

To a much smaller extent, the position of the metal–metal absorption band depends on the particle size. Colloidal suspensions of nickel 4-methylnioxime were prepared at various temperatures, and it was found that the position of the metal–metal absorption band undergoes a bathochromic shift of about 1 mμ per 10° increase in the temperature at which precipitation was caused to take place. It also was found that increasing the size of the colloidal particles, by digesting the suspension for 1 hr. at 80–90°, shifts the absorption band from 547 to 560 mμ. Shorter digestion times result in correspondingly smaller shifts. These results are probably associated with the Christiansen effect in which colloidal particles selectively scatter light on the long wave length side of an absorption band and thus shift the band to longer wave lengths. On the other hand, light of shorter wave lengths should be scattered more effectively, but it was observed that an absorption band at 399 mμ in nickel 4-methylnioxime was unaffected by digesting the precipitate.

The absorption of nickel 4-methylnioxime suspended in solvents such as diethyl ether, methanol, toluene, amyl alcohol and 1,2-dibromoethane was also investigated. The band due to the metal–metal bonds varied from 550 to 585 mμ while the band at 399 mμ did not shift. There is no obvious connection between the position of this band and the index of refraction of the solvent.

It was found that mixed crystals of the nickel, palladium and platinum complexes of 4-methylnioxime could be prepared. The absorption spectra of mixed crystals in colloidal suspension were compared with mechanical mixtures of the two complexes. These data are reported in Table II for a series of mixed crystals of nickel and palladium, along with the positions of maximum absorption of some mixed crystals with platinum. It will be noticed that in the mixed crystal a single absorption band is observed which lies between those of the pure complexes; whereas, in the mechanical mixture, two absorption bands are observed, one due to each of the complexes present.

TABLE II

ABSORPTION BANDS OF MIXED CRYSTALS OF Ni(II), Pd(II) AND Pt(II) COMPLEXES OF 4-METHYLNIOXIME IN COLLOIDAL SUSPENSION

Ratio Ni:Pd:Pt	Mixed crystal λ_{max}, mμ	Mechanical mixture λ_{max}, mμ
5:0:0	547	547
4:1:0	544	547, 470
3:2:0	534	547, 470
2:3:0	530	547, 470
1:4:0	510	547, 470
0:5:0	470	470
0:0:1	660	
0:1:2	580	
0:2:1	520	
1:0:3	630	
1:0:1	600	
3:0:1	570	
1:1:1	570–630[a]	

[a] Does not show a sharp maximum, but a very broad band.

Absorption Spectra of Single Crystals.—The absorption band due to metal–metal bonds causes dichroism in crystals of these complexes. In Fig. 3 the absorption spectra of crystals of nickel dimethylglyoxime, nickel nioxime and nickel heptoxime are reproduced. Plane polarized light was used. For each crystal the spectrum was measured with the electric vector of the polarized light parallel, ||, and perpendicular, ⊥, to the plane of the molecules in the crystal. The intensity of absorption is unknown because the thicknesses of the crystals were not measured. However, for each crystal the two curves are comparable as the same crystal was used.

The effect of the metal–metal bond length on the dichroism is readily apparent. Nickel dimethylglyoxime and nickel nioxime, which have the strongest (shortest) metal–metal bonds, show the greatest "abnormal" dichroism. In "normal" complexes maximum absorption occurs when the electric vector of the polarized light lies in the plane of the molecules in the crystal. On the other hand, nickel heptoxime has the weakest (longest) nickel–nickel bonds, and in this complex the dichroism is practically "normal."

The absorption spectra of single crystals of nickel α-furildioxime and nickel α-benzildioxime were also measured. The spectra of nickel α-benzildioxime show the presence of metal chains.

In the colloidal suspensions it was shown that the metal–metal absorption band in nickel α-furildioxime is almost obscured by a more intense band that is probably due to conjugation of the *vic*-dioxime with the aromatic groups. In the spectra of the crystal of nickel α-furildioxime this situation gives rise to "normal" dichroism, even though fairly strong metal–metal bonds are present.

In Table III the dichroism of some nickel and palladium complexes, as observed through a polarizing microscope, is given. Among the nickel complexes it will be seen that the colors listed in this table agree with the absorption spectra of the crystals. It should also be noted here that the dichroism of palladium heptoxime indicates the presence of metal–metal bonding because more blue light is absorbed when the electric vector of the polarized light is perpendicular to the plane of the molecules in the crystal.

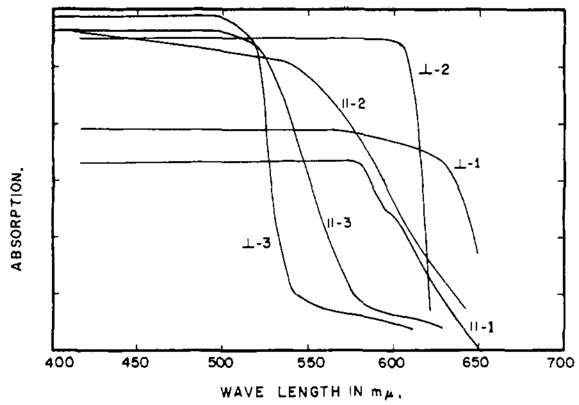

Fig. 3.—Absorption spectra of a single crystal of nickel dimethylglyoxime (curves ||-1 and ⊥-1), nickel nioxime (curves ||-2 and ⊥-2), and nickel heptoxime (curves ||-3 and ⊥-3). Curves ||-1, ||-2 and ||-3, electric vector of polarized light in plane of molecules; curves ⊥-1, ⊥-2 and ⊥-3, electric vector of polarized light perpendicular to plane of molecules.

TABLE III

METAL–METAL BOND LENGTHS AND DICHROISM OF METAL-(II)–*vic*-DIOXIME COMPLEXES

Complex	–M–M– bond length, A.	Color obsd. for indicated orientation of electric vector of polarized light relative to plane of molecule ||	⊥
Nickel dimethylglyoxime	3.233	Red	Dark red
Nickel nioxime	3.237	Red	Dark red
Nickel α-furildioxime	3.448	Very dark red	Dark red
Nickel α-benzildioxime	3.547	Yellow	Orange
Nickel heptoxime	3.596	Orange	Yellow
Palladium dimethylglyoxime	3.253	Yellow	Red
Palladium nioxime	3.250	Orange	Red
Palladium α-furildioxime	3.459	Red	Orange
Palladium α-benzildioxime	3.517	Dark yellow	Yellow
Palladium heptoxime	3.329	Light yellow	Yellow

There seems to be no satisfactory explanation for the difference between the absorption spectrum of the colloidal suspension and that of a single crystal of the same complex (compare nickel heptoxime in Fig. 1 and 3). The colloidal particles were shown by electron microscope measurements to be about 2000 Å. long so that each row of metal atoms contains about 600 atoms. According to Rundle[12] this is essentially an infinite chain so far as the band structure of the crystal is concerned, and, therefore, it should interact with light in the same manner as the very large crystals. This observed difference between the absorption spectrum of the colloidal suspension and that of the single crystal may be connected with the fact that in the colloidal suspension the crystals are oriented in all possible directions with respect to the light beam while in measurements with the single crystals they were always perpendicular to the light beam.

Acknowledgment.—The authors are indebted to

R. E. Rundle for many helpful discussions and suggestions during the course of this work and to D. T. Hooker for the work on the effect of particle size, suspending medium and mixed crystal formation on the absorption spectra.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF ATOMICS INTERNATIONAL, A DIVISION OF NORTH AMERICAN AVIATION, INC.]

Solid Phase Transitions in the UO_2–ZrO_2 System[1]

BY GERARD M. WOLTEN

RECEIVED FEBRUARY 26, 1958

Several aspects of the UO_2–ZrO_2 system have been studied and the following conclusions reached: At 2300°, the UO_2–ZrO_2 system consists of a homogeneous phase extending from 0 to 100 mole % ZrO_2. The crystal structure of this phase changes in a continuous manner from cubic for pure UO_2 to tetragonal for ZrO_2 rich mixtures. At temperatures above 2200°, the structure remained cubic for samples of increasing ZrO_2 content until 53–54 mole % ZrO_2 was reached, at which point the tetragonal structure was first recognized. The temperature at which pure zirconia transforms from a monoclinic to a tetragonal structure is lowered drastically by additions of urania, to the extent of approximately 100° per mole % UO_2 added.

Introduction

A phase diagram for the UO_2–ZrO_2 system has been reported,[2] but several important aspects of the system are still in doubt or unknown. In this investigation, information was obtained relative to the following three aspects: (1) the effect of UO_2 additions on the monoclinic-to-tetragonal transformation temperature of ZrO_2, (2) phase relationships in the binary system above 1950°, (3) the probable number of allotropic modifications of zirconia.

Experimental

The effect of urania additions on the monoclinic-to-tetragonal inversion of zirconia was investigated by X-ray diffraction of specimens containing varying amounts of UO_2 in a high-temperature Geiger counter diffractometer.[3] The specimens were solid solutions, prepared by sintering the appropriate mixtures at approximately 2000°. The intensity of the monoclinic 111 line was measured as a function of the temperature and interpreted as a measure of the amount of the monoclinic phase present.

In order to investigate the phase relationships above 2000°, mixtures of UO_2 and ZrO_2 of known composition were compressed into high-density tablets and heated under a reduced pressure of argon to 2300 ± 100° for 2 hr. They were then quenched to room temperature. The furnace and quenching apparatus are described elsewhere.[4] Since at these high temperatures, the vapor pressure of UO_2 is of the order of a micron,[5] the surfaces of the specimens lost considerable amounts of UO_2. Although the resulting concentration gradients appeared to be large only in the outer layers of the specimens, a successful effort was made to suppress the loss of UO_2 by wrapping the tablets tightly in tantalum foil. This resulted in homogeneous specimens which were suitable for bulk chemical analysis, so that a reliable correlation between composition and lattice parameters could be obtained.

Results and Discussion

On crystallographic grounds, urania would be expected to be more soluble in the tetragonal form of zirconia than in the monoclinic form and hence should lower the transformation temperature. This was found to be the case. The effect is very drastic and comparable in magnitude to that caused by yttria.[6]

The monoclinic-to-tetragonal transformation for 100% ZrO_2 has been reported[7,8] to occur over a range of temperatures and to exhibit hysteresis. This was found to be the case also for the compositions examined in this work, but the X-ray method permitted the beginning of the forward transformation on heating to be clearly recognized. A typical plot of intensity *vs.* temperature is shown in Fig. 1, for a sample containing 5 mole % UO_2. The intensity of the 111 line remained constant up to a certain temperature and then declined linearly with further increases in temperature; while simultaneously, the tetragonal pattern appeared and became more intense. The sharp break in the plot of the monoclinic 111 line intensity *vs.* the temperature was taken as the beginning of the transformation under the conditions of the experiment, and the corresponding temperatures for several different compositions are listed in Table I.

TABLE I

TEMPERATURE OF INCIPIENT MONOCLINIC-TO-TETRAGONAL TRANSFORMATION AS A FUNCTION OF COMPOSITION

Mole % UO_2	Temp., °C.
0 (pure ZrO_2)	1100 [7]
2	910
5	540
10	~0[a]
15	≪0[b]

[a] Both phases present at room temperature. [b] Specimen entirely tetragonal at room temperature.

In the investigation of binary phase relationships above 2000°, it was found that none of the samples showed the presence of more than one phase, although urania has a cubic crystal structure (fluorite type), while the high temperature form of zirconia is tetragonal (slightly distorted fluorite structure of axial ratio 1.018).

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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[5] R. J. Ackerman, "The High-Temperature, High-Vacuum Vaporization and the Thermodynamic Properties of Uranium Dioxide," ANL-5482, 1955, p. 82.

[6] P. Duwez, F. H. Brown, Jr., and F. Odell, *J. Electrochem. Soc.*, **98**, 356 (1951).

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