TABLE V

BAND ASSIGNMENTS OF BIS(ACETYLACETONATO)PLATINUM(II) AND ITS DEUTERATED ANALOGS

1:1	1:2			
d_0 compound	d_0 compound	d_2 compound	d_{14} compound	Predominant mode
1563 s	1568 s	1560 s	1550 s	$C\overset{...}{-}O$ str
1538 s	1544 s	1501 s	1500 s	$C\overset{...}{-}C$ str
1429 m	1425 sh	1425 sh	1060 w	CH_3 deg def
1380 s	1405 s	1390 s	1395 s	C—O str
1363 sh	1375 m	1367 m	1029 m	CH_3 sym def
1288 m	1283 m	1283 m	1303 m	$C\overset{...}{-}C$ str
			1275	
1222 w	1204 w	885 vw	865 vw	C—H bend
1033 m	1027 m	1030 m	946 m	CH_3 rock
1018 m				
952 m	945 m	954 m	946 m	C—CH_3 str
941 m		923 w	919 w	
817 s	779 s	582 s	581 s	π (C—H)
703 w	712 m	710 m	...	Pt—O str + ring def
650 s	690 s	688 s	688 s	Pt—O str
...	660 w	672 w	670 w	...
478 m	479 s	475 s	476 s	Pt—O str
448 m	452 m	444 m	444 m	Ring def
283 w	279 m	279 m	279 m	C—CH_3 bend
	272 sh	272 sh	260 sh	

the present work, we have carried out a similar calculation using the modified force field described above. It was found that both calculations give essentially similar results for the high-frequency bands as well as for the low-frequency bands concerning the C–CH_3 bending and ring deformation modes. Although the errors in coordinate bond stretching frequencies are about 10%, this may be improved by increasing the force constant by 15–20%. A satisfactory result can, therefore, be obtained by using the 1:1 approximation within these restrictions.

In view of the present results, the following modifications of the previous band assignments[8] may be suggested: (1) The band assignments for the $C\overset{...}{-}O$ and $C\overset{...}{-}C$ stretching bands above 1500 cm^{-1} should be interchanged. (2) The band assignments for the CH_3 degenerate deformation and the lower frequency $C\overset{...}{-}O$ stretching should also be interchanged.

More accurate analysis of the 1:2 and 1:3 compound spectra, especially in the low-frequency region, must await a complete normal coordinate treatment considering the entire molecule.

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Infrared Spectra and Structure of Acetylacetonato Platinum(II) Complexes. II. Infrared Spectra and Normal Coordinate Analysis of Sodium Dichlorobis(γ-acetylacetonato)platinate(II)[1]

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The infrared spectra of sodium dichlorobis(γ-acetylacetonato)platinate(II) and two of its deuterated analogs have been obtained in the region 4000 to 200 cm^{-1}. Normal coordinate analyses have been carried out on these three species using a simplified molecule model. A Urey–Bradley force field was used to determine the force constants, particularly for the platinum–carbon stretching vibration. The value of 2.50 mdynes/A thus determined is compared with other platinum coordinate bond stretching force constants. Force constants and band assignments and their relation to structure are discussed.

Introduction

Several complexes of platinum(II) first prepared by Werner[3] were reported to contain acetylacetone as a unidentate ligand. It has been shown recently that in these complexes platinum is bonded to the γ-carbon atom of acetylacetone.[4–7] The unusual stability of these platinum–carbon bonds is indicated by their formation in strongly basic aqueous solutions.

The infrared spectra of metal acetylacetonato complexes have been studied by several investigators,[8] and we have recently carried out a complete normal coordinate analysis on a simple bidentate oxygen-bonded platinum complex, potassium dichloro(acetylacetonato)platinate(II),[9] for which the Urey–Bradley force field was found to be inadequate to describe the observed spectra due to interactions between resonance forms.

The possible existence of carbon-bonded metal acetylacetonates prompted us to extend our study of

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[2] To be submitted by G. T. B. to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. Werner, *Ber.*, **34**, 2584 (1901).

[4] G. Allen, J. Lewis, R. F. Long, and C. Oldham, *Nature*, **202**, 589 (1964).

[5] B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *ibid.*, **195**, 1278 (1962).

[6] J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).

[7] R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 1472 (1964).

[8] For example, see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 216.

[9] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

infrared spectra to include these platinum–carbon bonded forms; in particular, to perform a normal coordinate analysis to assist in making infrared band assignments and to thus facilitate the identification of structures of this type using infrared spectroscopy. This type of study is highly desirable since, thus far, only empirical band assignments are available for the C-bonded $Na_2[Pt(acac)_2]Cl_2 \cdot 2H_2O$.[6] Information on the magnitude of the Urey–Bradley stretching, bending, and repulsive force constants of complexes containing platinum–carbon bonds is not at present available for any but the simplest structures.

In the present investigation we have prepared the complexes of the type $Na_2[Pt(acac)_2Cl_2] \cdot 2H_2O$ in which acetylacetone is unidentate and bonded to the platinum through the γ-carbon atom. The infrared spectra in the region 4000 to 200 cm^{-1} have been obtained for this molecule and two of its deuterated analogs. A normal coordinate analysis has been carried out using a Urey–Bradley force field. The results obtained for the nondeuterated complex were confirmed by extending similar calculations to the deuterated compounds.

Experimental Section

Preparation of the Compounds.—Sodium dichlorobis(γ-acetylacetonato)platinate(II)·$2H_2O$ was prepared by dissolving 5 g (12.0 mmoles) of potassium tetrachloroplatinite(II) in 15 ml of warm water and adding 10.0 ml (97.6 mmoles) of acetylacetone with 7.0 ml of 12.5 *M* sodium hydroxide. After shaking for a few minutes a copious bright yellow precipitate formed which was separated immediately by vacuum filtration. The crude material was recrystallized from a dilute sodium hydroxide solution to prevent decomposition. The product was washed with alcohol and ether with some resultant loss of water and dried over P_2O_5. The product was decomposed by dilute HCl to give acetylacetone, and 2,4-dinitrophenylhydrazone derivatives were formed which were not further characterized. *Anal.* Calcd for $C_{10}H_{18}O_6Cl_2PtNa_2$: C, 21.99; H, 3.32; Cl, 12.98. Found: C, 22.17; H, 3.29; Cl, 12.66.

Sodium dichlorobis(γ-acetylacetonato-d_1)platinate (II)·$2D_2O$ was prepared in a manner analogous to that of the nondeuterated analog, using D_2O as the solvent and acetylacetone-d_2 prepared as previously described.[9]

Sodium dichlorobis(γ-acetylacetonato-d_7)platinate(II)·$2D_2O$ was prepared as above using completely deuterated acetylacetone prepared by exchange in potassium carbonate as previously described.[9]

The degree of isotopic substitution was verified by nmr spectra of both deuterated ligands and chelates. Both D_2O and dimethyl sulfoxide-d_6 were found to be adequate nmr solvents for the chelates.

Spectral Measurements

The spectra between 4000 and 200 cm^{-1} were measured with a Beckman IR-12 infrared spectrophotometer. The KBr disk method was employed for the region 4000 to 650 cm^{-1}. From 650 to 200 cm^{-1}, polyethylene pellets prepared as previously described[9] were employed. Calibration of the frequency readings was made with polystyrene film, 1,2,4-trichlorobenzene, and water vapor.

Method of Calculation

The molecular model chosen for this simplified calculation is shown in Figure 1, in which R is methyl and is treated as a single atom having a mass of 15.035. Figure 1 also shows the 20 internal coordinates used for the calculation. This nine-atom model will have 21 normal vibrations which may be classified into two species, 12 A′ and 9 A″, under C_s symmetry. Each of these two species contains two torsional modes which are expected to occur at very low frequencies, certainly below the range for which experimental data are available. Accordingly, our calculation was simplified by deleting those internal coordinates corresponding to torsion. The remaining 10 A′ and 7 A″ vibrations are the subject of this paper. Some other vibrational modes of the entire complex ion are not included in the molecular model. Of these, the platinum–chlorine stretching band is the only one within the range of experimental observation and can be assigned empirically. The remaining bending modes involving the coordinate bonds are therefore not calculated for the same reason given above for torsions.

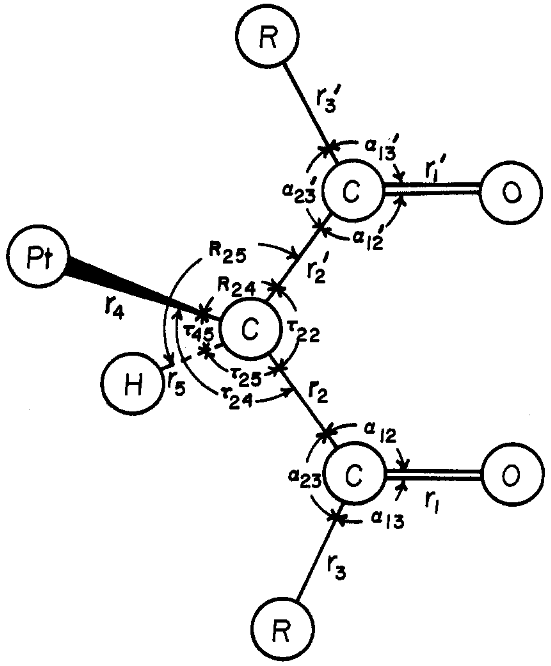

Figure 1.—Molecular model and internal coordinates.

The *G* matrix was formed using the methods outlined by Wilson, Decius, and Cross.[10] The *G* matrix elements were evaluated using the following molecular parameters: $r_1 = r_1' = 1.20$ A, $r_2 = r_2' = 1.54$ A, $r_3 = r_3' = 1.58$ A, $r_4 = 2.13$ A, $r_5 = 1.08$ A, $\alpha_{12} = \alpha_{12}' = \alpha_{23} = \alpha_{23}' = \alpha_{31} = \alpha_{31}' = 120°$, $\tau_{22} = \tau_{45} = \tau_{25} = \tau_{24} = R_{24} = R_{25} = 109° 28'$. They are similar to those obtained from the X-ray analysis of $K[Pt(acac)_2Cl]$,[5] in which one acetylacetone ligand is bidentate and the other coordinated through the central carbon. They are in agreement with the covalent radii of Pauling.[11] The angles around the γ carbon were chosen as the appropriate sp^3 angles of 109° 28′, since the position of the central hydrogen was not determined by the X-

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[10] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations—The Theory of Infrared and Raman Vibrational Spectra," McGraw-Hill Book Company, Inc., New York, N. Y., 1955.

[11] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

ray study. Small errors in these values are not expected to affect the result of this calculation significantly since the force constants are the most important factor in determining frequencies.

In order to express the F matrix, a Urey–Bradley force field[12] was employed. The G and F matrices thus obtained contain three angle redundancies. These angle redundancies were removed using simple trigonometric relationships. The resultant symmetry coordinates are shown in Table I. The remaining 10th order A′ and 7th order A″ secular equations of the form $|GF - E\lambda| = 0$ were solved using an IBM 7094 computer.

Table II lists the set of force constants which give the best fit to the observed frequencies of the three isotopic species. Table III compares the observed frequencies with those calculated by using the set of force constants shown in Table II. Agreement is quite satisfactory, the maximum error being about 5% (ν_{16} of d_7 compound). The last column of Table III gives the theoretical band assignments obtained from the calculation of the potential energy distribution shown in Table IV.

TABLE I

SYMMETRY COORDINATES

Species	Symmetry coordinate	Vibrational mode[a]
A′	$S_1 = (1\sqrt{2})(\Delta r_1 + \Delta r_1')$	CO str
	$S_2 = (1/\sqrt{2})(\Delta r_2 + \Delta r_2')$	CC str
	$S_3 = (1/\sqrt{2})(\Delta r_3 + \Delta r_3')$	CR str
	$S_4 = \Delta r_4$	PtC str
	$S_5 = \Delta r_5$	CH str
	$S_6 = (1/2)(\Delta\alpha_{13} + \Delta\alpha_{13}' - \Delta\alpha_{23} - \Delta\alpha_{23}')$	CR bend
	$S_7 = (1/\sqrt{12})(2\Delta\alpha_{12} + 2\Delta\alpha_{12}' - \Delta\alpha_{23} - \Delta\alpha_{23}' - \Delta\alpha_{13} - \Delta\alpha_{13}')$	Skeletal bend
	$S_8 = (1/\sqrt{20})(4\Delta\tau_{22} - \Delta\tau_{24} - \Delta\tau_{25} - \Delta R_{24} - \Delta R_{25})$	CCC bend
	$S_9 = (1/\sqrt{30})(-\Delta\tau_{22} - \Delta\tau_{24} - \Delta\tau_{25} - \Delta R_{24} - \Delta R_{25} + 5\Delta\tau_{45})$	PtCH bend
	$S_{10} = (1/2)(\Delta\tau_{24} + \Delta R_{24} - \Delta\tau_{25} - \Delta R_{25})$	PtC(acac) bend
A″	$S_1' = (1/\sqrt{2})(\Delta r_1 - \Delta r_1')$	CO str
	$S_2' = (1/\sqrt{2})(\Delta r_2 - \Delta r_2')$	CC str
	$S_3' = (1/\sqrt{2})(\Delta r_3 - \Delta r_3')$	CR str
	$S_4' = (1/2)(\Delta\alpha_{13} - \Delta\alpha_{13}' + \Delta\alpha_{23}' - \Delta\alpha_{23})$	CR bend
	$S_5' = (1/\sqrt{12})(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{13} - 2\Delta\alpha_{12}' + \Delta\alpha_{23}' + \Delta\alpha_{13}')$	Skeletal bend
	$S_6' = (1/2)(\Delta\tau_{24} + \Delta\tau_{25} - \Delta R_{24} - \Delta R_{25})$	CH bend
	$S_7' = (1/2)(\Delta\tau_{24} - \Delta\tau_{25} - \Delta R_{24} + \Delta R_{25})$	PtC(acac) bend

[a] R denotes the CH_3 group.

TABLE II

FORCE CONSTANTS FOR SODIUM DICHLOROBIS(γ-ACETYLACETONATO)PLATINATE(II) (MDYNES/A)

(I) Stretching

$K(C{=}O) = 8.84$

$K(C{-}C) = 2.52$

$K(C{-}R) = 3.85$

$K(Pt{-}C) = 2.50$

$K(C{-}H) = 4.48$

(II) Bending

$H(O{-}C{-}C) = 0.38$

$H(C{-}C{-}R) = 0.49$

$H(O{-}C{-}R) = 0.27$

$H(C{-}C{-}C) = 0.16$

$H(Pt{-}C{-}C) = 0.15$

$H(H{-}C{-}C) = 0.20$

$H(H{-}C{-}Pt) = 0.04$

(III) Repulsive

$F(C\cdots O) = 0.40$

$F(C\cdots R) = 0.60$

$F(O\cdots R) = 0.37$

$F(C\cdots C) = 0.47$

$F(C\cdots Pt) = 0.27$

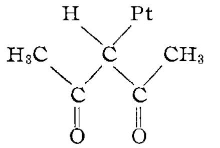
$F(C\cdots H) = 0.36$

$F(Pt\cdots H) = 0.20$

Results and Discussion

(I) Band Assignments.—A comparison of the infrared spectra (2000–200 cm^{-1}) of sodium dichlorobis(γ-acetylacetonato)platinum(II) dihydrate and its deuterated analogs is shown in Figure 2. The spectra above 2000 cm^{-1} are not shown because there are no significant absorptions except C–H (or C–D) stretching and O–H stretching of crystal water. Water is evidently not coordinated to the metal, as evidenced by the broadness of the band in the O–H stretching region.

The relatively high frequency of the symmetric (ν_2) and asymmetric (ν_{11}) C=O stretching bands is the most characteristic feature of this class of compounds. They are found at 1650 and 1626 cm^{-1}, respectively, and are distinctly separated from the C—C stretching frequencies, in contrast to the oxygen-chelated forms, where these bands partially overlap.[9] The high frequency of the C=O stretching modes is evidence that the carbonyl groups are not interacting with the platinum and supports the choice of structure I, in which the oxygens are *cis* to each other. This structure is also supported by the X-ray analysis of $K[Pt(acac)_2Cl]$,[5] whose C-bonded acetylacetonato ligand exhibits two C=O stretching bands at 1695 and 1653 cm^{-1}. In Structure II, one of the C=O stretching bands may be shifted to a lower frequency because of a possible interaction between the oxygen and the platinum atoms. As is seen in Table III, ν_{11} is shifted by approximately 36 cm^{-1} to a lower frequency upon deuteration at the γ carbon. Although our calculation does not predict this shift, it may be due to a distortion of the tetrahedral angles around the γ carbon. Unfortunately, the position of the hydrogen on the γ carbon has not yet been determined by X-ray analysis.[5] The absence of the bands at 1550 and 1540 cm^{-1} reported by Wentworth and Brubaker[7] is noted.



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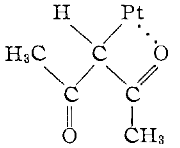

II

The central C–C stretching frequencies are found at 1350 (ν_3) and 1193 (ν_{12}) cm^{-1}. The large separation between these two modes is due to interaction between their adjacent internal coordinates. In addition, strong coupling is found, with the C–CH_3 stretching mode in ν_3. The methyl group vibrations which were not the subject of this calculation are easily identified by isotopic substitution and conform well with assignments made by group frequency techniques. The CH_3 degenerate and symmetric deformations at 1465 and 1433 cm^{-1}, respectively, disappear completely upon deuteration of the methyl groups and reappear at 1065 and 1032 cm^{-1}. The methyl rocking modes at 1024 and 1007

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(12) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

TABLE III

A COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES OF SODIUM DICHLOROBIS(γ-ACETYLACETONATO)PLATINUM(II) AND ITS DEUTERATED ANALOGS (cm^{-1})[a]

	d_0 compound		d_1 compound		d_7 compound		
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Predominant modes[b]
				A′ Species			
ν_1	...	2982	...	2185	...	2185	S_5
ν_2	1652 s	1650	1652 s	1648	1640 s	1646	S_1
ν_3	1350 s	1315	1363 s	1315	1360 s	1300	$S_2 + S_3$
ν_4	948 m	986	913 m	947	908 m	946	$S_8 + S_4 + S_2 + S_9$
ν_5	852 s	879	710 s	731	698 s	725	$S_8 + S_2 + S_3$
ν_6	652 s 648 sh	649	625 s 633 sh	627	606 s 588 sh	600	$S_4 + S_7 + S_3 + S_6$
ν_7	567 w	573	528 m	515	527 m	515	$S_4 + S_7$
ν_8	318 w	320	318 w	320	302 w	302	$S_6 + S_7$
ν_9	250 m	252	250 m	251	250 m	250	S_{10}
ν_{10}	...	131	...	131	...	127	$S_9 + S_8$
				A″ Species			
ν_{11}	1626 m	1626	1587 m	1624	1587 m	1623	S_1'
ν_{12}	1193 s	1247	1191 s	1230	1180 s	1222	$S_2' + S_6'$
ν_{13}	1193 s	1147	959 w	978	962 w	956	$S_6' + S_3'$
ν_{14}	901 m	884	780 m	768	780 m	758	$S_3' + S_6'$
ν_{15}	536 s	532	528 m	527	527 m	511	S_4'
ν_{16}	384 s	402	383 s	402	376 s	396	S_5'
ν_{17}	211 m	215	211 m	214	210 m	211	S_7'
				Not Calculated			
	1465 s		1450 s		1065 m		CH_3 deg def
	1433 sh		1440 sh		1032 m		CH_3 sym def
	1024 m		1024 m		927 m		CH_3 rock
	1007 m		1007 m		908 m		CH_3 rock
	327 m		327 m		327 m		PtCl str

[a] s, strong; m, medium; w, weak; sh, shoulder. [b] Refers to nondeuterated compound.

TABLE IV

THE POTENTIAL ENERGY DISTRIBUTION FOR SODIUM DICHLOROBIS(γ-ACETYLACETONATO)PLATINATE(II)[a]

A′ Species

Symmetry coordinate		Observed frequency (cm^{-1})								
	2982[b]	1652	1350	948	852	652	567	318	250	131[b]
S_1	0.00	*1.00*	0.08	0.11	0.06	0.00	0.00	0.01	0.00	0.00
S_2	0.01	0.01	*1.00*	*0.85*	*0.61*	0.09	0.06	0.05	0.01	0.00
S_3	0.01	0.05	*0.77*	0.27	*0.48*	*0.47*	0.00	0.02	0.00	0.00
S_4	0.02	0.00	0.04	*0.98*	0.00	*1.00*	*1.00*	0.00	0.03	0.00
S_5	*1.00*	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00
S_6	0.00	0.00	0.11	0.00	0.00	*0.37*	0.13	*1.00*	0.02	0.05
S_7	0.00	0.01	0.12	0.08	0.19	*0.48*	*0.55*	*0.34*	0.03	0.01
S_8	0.00	0.00	0.00	*1.00*	*1.00*	0.16	0.13	0.01	0.03	*0.40*
S_9	0.00	0.00	0.00	*0.45*	0.23	0.06	0.17	0.00	0.19	*1.00*
S_{10}	0.00	0.00	0.00	0.09	0.05	0.00	0.08	0.00	*1.00*	0.17

A″ Species

	Observed frequency (cm^{-1})						
	1626	1193	1193	901	536	384	211
S_1'	*1.00*	0.03	0.01	0.06	0.00	0.00	0.00
S_2'	0.00	*1.00*	0.05	0.30	0.01	0.03	0.00
S_3'	0.00	0.18	*0.33*	*1.00*	0.06	0.00	0.00
S_4'	0.01	0.00	0.09	0.00	*1.00*	0.02	0.01
S_5'	0.00	0.04	0.00	0.00	0.03	*1.00*	0.01
S_6'	0.00	*0.38*	*1.00*	*0.54*	0.01	0.00	0.03
S_7'	0.00	0.00	0.03	0.03	0.00	0.02	*1.00*

[a] If there are more than two relatively large contributions, only the term which contributes more than 0.3 is used to represent the vibrational coupling. [b] Calculated frequency (cm^{-1}).

cm^{-1} are similarly found to shift to 927 and 908 cm^{-1}. The band at 901 cm^{-1} (ν_{14}) is due to the C–CH_3 stretching coupled with the CH bending mode (S_6'). However, the band at 948 cm^{-1} (ν_4) contains significant contributions from the C–C–C bending (S_8), Pt–C stretching (S_4), and C–C stretching (S_2). The band at 852 cm^{-1} (ν_5) is due to the C–C–C bending coupled with the C–C and C–CH_3 stretching.

As seen in Table IV, a strong band at 652 cm^{-1} (ν_6), with a shoulder at 648 cm^{-1}, again contains contribu-

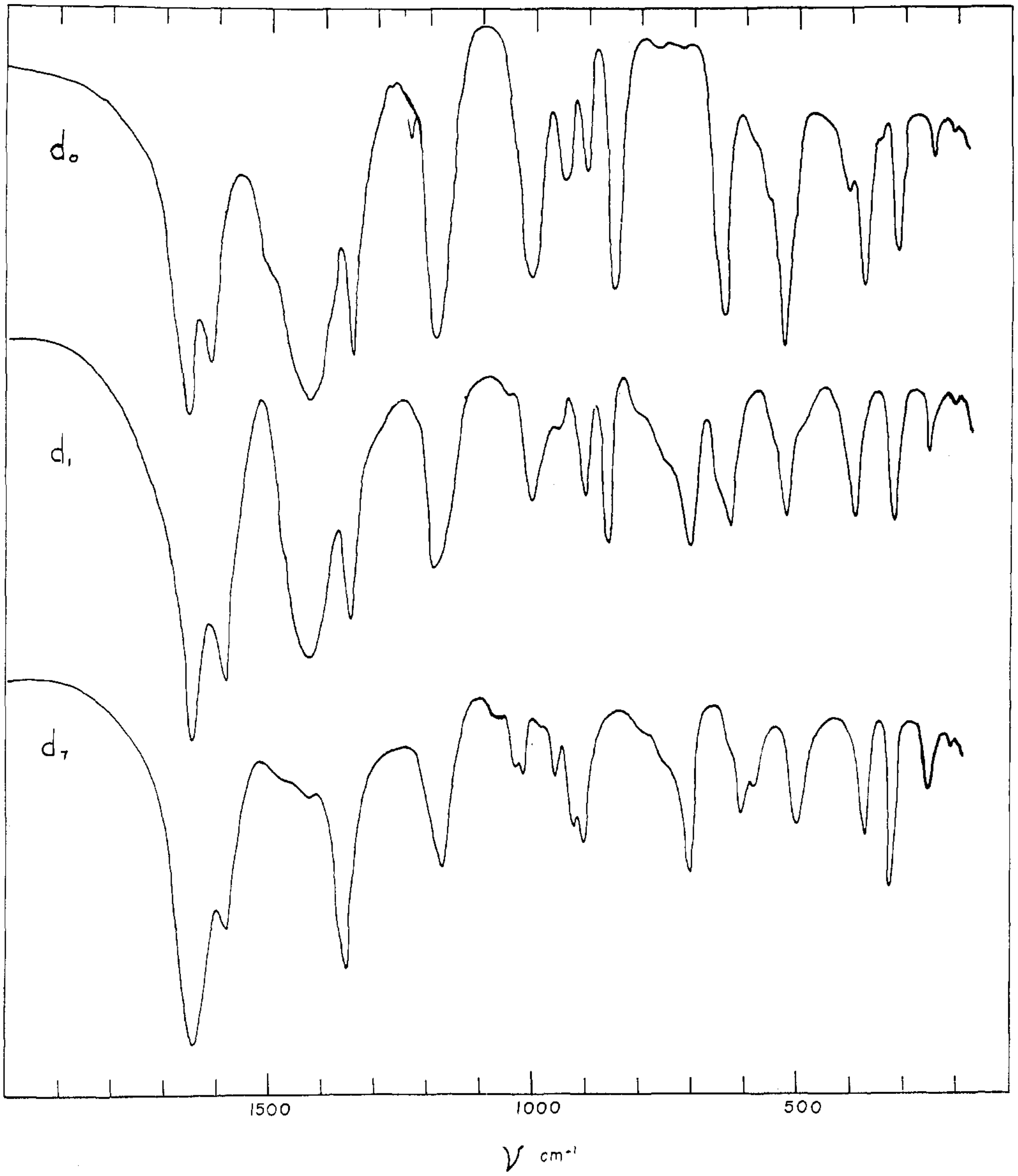

Figure 2.—Infrared spectra of sodium dichlorobis(γ-acetylacetonato)platinum(II) dihydrate and its deuterated analogs.

tions from several vibrational modes. A weak band at 567 cm^{-1} (ν_7) is mainly due to the Pt–C stretching mode. This frequency is in excellent agreement with that of the Pt–C stretching mode reported for hydroxytrimethylplatinum(IV).[13] A strong band at 536 cm^{-1} of d_0 is assigned to the C–CH$_3$ bending mode (ν_{15}). This band is overlapped with ν_7 in the d_1 and d_7 compounds. A skeletal bending (ν_{16}) appears strongly at 384 cm^{-1}, and it is sensitive to the deuteration of the CH$_3$ groups. The next band, at 327 cm^{-1}, is assigned empirically to the Pt–Cl stretching mode. The absence of a strong doublet structure in this band (found in *cis*-dichloro Pt(II) compounds[9]) is indicative of a *trans*-dichloro structure. This is also supported by the small value of the dielectric constant obtained in dioxane solution. A weak shoulder band at 318 cm^{-1} was assigned to the C–CH$_3$ bending coupled with a skeletal bending mode (ν_8). The bands at 250 and 211 cm^{-1} are assigned to two Pt–C(acac) bendings which involve the motion of the whole ligand about the Pt atom. Finally, ν_{10} (Pt–CH bending plus C–C–C bending) was calculated at 131 cm^{-1} below the range of our observation.

(II) **Force Constants.**—The force constants used to give the best fit to the observed frequencies are shown in Table II. The carbonyl stretching force constant of 8.84 mdynes/A is somewhat smaller than that found for acetone (10.5 mdynes/A).[14] This indicates a small amount of delocalization along the carbon chain connecting the two carbonyl groups and is supported by the somewhat higher frequencies of these C–C stretching modes. As noted previously,[9] the value of 3.85 mdynes/A given to K(C–CH$_3$) in our approximation includes the carbon–hydrogen repulsions of each of the methyl hydrogens. If it is assumed that the repulsive force constant of 0.36 mdyne/A is representative of the

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(13) G. L. Morgan, R. D. Rennick, and C. C. Soong, *Inorg. Chem.*, **5**, 372 (1966); D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, **21**, 327 (1965).

(14) S. Mizushima and T. Shimanouchi, "Infrared Absorption and Raman Effect," Kyoritsu, Tokyo, 1958.

magnitude of this interaction,[9] simply subtracting the three CH repulsions would reduce the stretching force constant to 2.77 mdynes/A. This is more nearly comparable to the value of 2.52 mdynes/A found for the central C–C stretching force constant.[14]

The value of 2.50 mdynes/A for K(Pt–C) is very similar to that of 2.46 mdynes/A for K(Pt–O) previously determined.[9] This result is at least consistent with the chemical observation that both types of coordinate bonds are formed not only under the same conditions but also in the same reaction mixture.[3] This result may suggest that the order of the strength of these coordinate bonds[9] may be Pt–CN ≫ Pt–C(acac) ≈ Pt–O(acac) > Pt–NH_3.

The bending and repulsive force constants are similar to those obtained previously.[9] The changes observed are those expected due to changes in structure. For example, the value of 0.26 mdyne/A used previously for $H(\mathrm{C}\cdots\mathrm{C}\cdots\mathrm{C})$ was reduced to 0.16 mdyne/A in this case.

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Complexes of Bivalent Iron, Cobalt, Nickel, and Copper with Bis(2-dimethylaminoethyl) Oxide

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The potentially tridentate ligand bis(2-dimethylaminoethyl) oxide (Me_4daeo) forms 1:1 complexes with the chlorides and bromides of Fe(II), Co(II), Ni(II), and Cu(II). Spectral, conductivity, and molecular weight data indicate that these complexes have the discrete molecular structure M(Me_4daeo)X_2 both in solution and in the solid state. The crystal field spectra of these complexes strongly suggest a full fivefold coordination of the metal ions. The 1:1 compounds of $Co(NCS)_2$ and $Ni(NCS)_2$ with the ligands Me_4daeo and bis(2-dimethylaminoethyl)methylamine have been prepared and studied. All of the above compounds have values of the magnetic moment typical of a high-spin configuration.

Introduction

Recently several papers have dealt with five-coordinated complexes of the bivalent metals of the first transition group. When the ligands contain donor atoms such as nitrogen and oxygen, high-spin complexes are obtained.[1–4] On the other hand, with ligands containing donor atoms with a low electronegativity, as is the case with phosphines, arsines, isonitriles, and ligands containing sulfur, the compounds are of the low-spin type.[5]

The steric requirements of the ligands and the nature of the donor atoms both appear to be critical factors in determining whether a five-coordinated structure is attained instead of a four- or six-coordinated structure. In order to vary both of these factors systematically we have now prepared a series of compounds formed from the potentially tridentate ligand $O[CH_2CH_2N(CH_3)_2]_2$, bis(2-dimethylaminoethyl) oxide (Me_4daeo), with the salts MX_2, where M = the transition ions between Fe and Cu and X = Cl, Br, or NCS. This ligand is structurally similar to $CH_3N[CH_2CH_2N(CH_3)_2]_2$, hereafter abbreviated as Me_5dien, which forms five-coordinated complexes with the metals mentioned above.[3] It is also similar to $HN[CH_2CH_2N(C_2H_5)_2]_2$, hereafter abbreviated as Et_4dien, which, as Dori and Gray have shown, forms five-coordinated complexes with cobalt(II) and four-coordinated planar complexes (one free X^-) with nickel(II) in the solid state.[4] Compared with Me_5dien and Et_4dien, Me_4daeo appears to be a less bulky ligand. The oxygen of the ether group is not usually a good donor atom but when it is part of chelate ligands it has been shown to coordinate with 3d metal ions.[6]

Experimental Section

Materials.—All solvents were of reagent grade quality. 1,2-Dichloroethane was washed with 5% aqueous sodium hydrogen carbonate, dried for 24 hr over anhydrous calcium chloride, and fractionally distilled.

Preparation of the Compounds.—The preparation of bis(2-dimethylaminoethyl) oxide was accomplished by methylation of bis(2-aminoethyl) oxide with a HCOOH–HCHO mixture. After the evolution of carbon dioxide had practically stopped, all of the volatile fractions were removed by vacuum distillation. The solid residue was treated with a saturated solution of sodium hydroxide and the oily layer formed was extracted into ether. The ethereal extract was dried over potassium hydroxide. After removal of the ether the compound bis(2-dimethylaminoethyl) oxide distilled as a colorless oil, bp 42° (1.5 mm). *Anal.* Calcd for $O[CH_2CH_2N(CH_3)_2]_2$: N, 17.48. Found: N, 17.61. Hot solutions of the appropriate metal salt (0.010 mole) in 1-butanol (60 ml) and bis(2-dimethylaminoethyl) oxide (0.012 mole) in 1-

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