and Ahrens[10] are for cations in 6-fold coördination while those of Bertaut and Forrat[9] are for 8-fold, and those of Geller[12] are for 12-fold coördination. No corrections in the above mentioned radii have been made for coördination.

The lattice constants found experimentally in this work and the deviations from constants calculated from referenced atomic radii are listed in Table II.

The data obtained with rare earth radii according to Templeton and Dauben[11] gives the closest agreement with experimentally determined lattice constants. Calculations based on the radii of Geller[12] and Ahrens[10] give fairly good agreement with experimental results. The radii of Bertaut and Forrat[9] give the poorest agreement.

The lattice constants calculated from equations 1 through 3 for each particular rare earth stannate are quite close, indicating that the ratios of analogous radii in each set are comparable. Thus the data support the conclusion that radius ratios for trivalent lanthanide ions are essentially unchanged by the particular coördination in the isostructural series used for radii determinations.

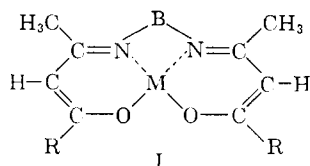[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Dipole Moments of Metal Chelate Compounds. IV. Metal Chelates of Analogs and Polar Substituted Analogs of Bisacetylacetoneethylenediimine[1,2]

BY RICHARD J. HOVEY AND ARTHUR E. MARTELL

The dipole moments of some copper(II) and nickel(II) chelates of the tetradentate Schiff base ligands, bis-*p*-bromobenzoylacetonepropylenediimine, bis-*m*-nitrobenzoylacetonepropylenediimine, bistrifluoroacetylacetonepropylenediimine, bisbenzoylacetonetramethylenediimine and bisbenzoylacetone-1,3-diimino-2-propanol and of the vanadyl complexes of dibenzoylmethane and bisbenzoylacetonepropylenediimine have been measured. The observed dipole moments of the metal chelates which contain highly polar substituents such as trifluoromethyl and *p*-bromophenyl groups agree approximately with the values calculated for the theoretical structures in which these groups occupy terminal positions. Differences between the observed and theoretical values have been interpreted as due to resonance interaction between the polar groups and the conjugated metal chelate rings. The large dipole moment value of bisdibenzoylmethano-oxovanadium(IV) is indicative of the ionic character of the vanadium–oxygen bond perpendicular to the plane of the chelate rings. This is further reflected in the dipole moment of bisbenzoylacetonepropylenediimino-oxovanadium(IV) which is approximately one and a half to two Debye units higher than the dipole moments of the other metal chelates of this ligand.

In an earlier paper[3] the electric dipole moments of metal chelates prepared from bisacetylacetoneethylenediimine and some of its analogs were reported. The purpose of the present investigation was primarily to observe the changes in dipole moments resulting from the introduction of polar groups such as p-C_6H_4Br, m-$C_6H_4NO_2$, OH and CH_3 into the chelate molecules. For this purpose the metal chelates represented by I and listed in Table I were synthesized[4] and their dipole moments were measured. In chelates containing (a) a benzoylacetone residue, R = C_6H_5, (b) a p-bromobenzoylacetone residue, R = p-C_6H_4Br, (c) a m-nitrobenzoylacetone residue, R = m-$C_6H_4NO_2$ and (d) a trifluoroacetylacetone residue, R = CF_3. Where the bridge is (a) propylenediimine, B = $CH(CH_3)$-CH_2, (b) tetramethylenediimine, B = $(CH_2)_4$ and (c) 1,3-diimino-2-propanol, B = $CH_2CH(OH)CH_2$.

The dipole moments of the ligands, from which the

metal chelates reported here were derived, have been reported in previous publications.[5,6]

Experimental

Procedure.—A description of the superheterodyne-beat apparatus and the procedure employed in measuring the dielectric constants of benzene solutions of the metal chelates have been given earlier.[5] The densities of these solutions were measured with a 25-ml. Rieschauer pycnometer. All measurements were carried out in a constant temperature oil-bath at 25°; for the determination of an individual dipole moment the temperature remained within ± 0.01°. The method of calculating the dipole moments from the experimental data and the significance of the parameters listed in Table I have also been given before.[5,7]

Induced Polarization.—Since all of the metal chelates reported here are highly colored, the molar refraction of each was taken as the sum of the individual bond refractions obtained from Vogel's table.[8] The molar refractions so calculated are considered to be quite reliable and differ from observed values usually by less than 1%.[9]

The atomic refractions used for four-coördinated copper (II) and nickel(II) are the same as those used by McCarthy and Martell[3] and are 14.5 ± 2 and 10.0 ± 2 cc., respectively. A value of 12 cc. has been allowed for both copper(II) and nickel(II) in similar four-coördinated complexes by Macqueen and Smith.[10] This represented the average difference between the observed molar refraction of several organic parent compounds and their corresponding metal chelates for which the measurements did not seem to be vitiated by anomalous dispersion.

No literature values are available on the atomic refraction of six-coördinated vanadium. However, the atomic refractions for four-coördinated Co, Ni, Cu and Pd range between 10 and 16 cc., with a general tendency for the

(1) Abstracted from a dissertation submitted by Richard J. Hovey to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1958.

(2) This work was sponsored by the Office of Ordnance Research under Contract No. DA-19-020-ORD-3243.

(3) P. J. McCarthy and A. E. Martell, THIS JOURNAL, **78**, 2106 (1956).

(4) R. J. Hovey, J. J. O'Connell and A. E. Martell, *ibid.*, **81**, 3189 (1959).

(5) P. J. McCarthy and A. E. Martell, *ibid.*, **78**, 264 (1956).

(6) R. J. Hovey and A. E. Martell, *ibid.*, **82**, 364 (1960).

(7) I. Halverstadt and W. Kumler, *ibid.*, **64**, 2988 (1942).

(8) A. Vogel, *Chem. & Ind. (London)*, 358 (1950).

(9) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(10) J. Macqueen and J. W. Smith, *J. Chem. Soc.*, 1821 (1956).

TABLE I

Compound	ϵ_1	α	v_1	$-\beta$	P_E(cc.)	$P_{2\infty}$(cc.)	μ(D.)
Bis-p-bromobenzoylacetonepropylenediiminocopper(II)	2.2701	10.560	1.14671	0.5356	134.86	1264.90	7.28
Bis-p-bromobenzoylacetonepropylenediiminonickel(II)	2.2717	10.419	1.14596	.5724	130.36	1231.05	7.19
Bis-m-nitrobenzoylacetonepropylenediiminonickel(II)	2.2724	19.763	1.14358	.4908	127.58	1990.08	9.43
Bistrifluoroacetylacetonepropylenediiminocopper(II)	2.2779	25.878	1.14547	.5189	79.09	2053.00	9.73
Bistrifluoroacetylacetonepropylenediiminonickel(II)	2.2787	23.658	1.14611	.4243	74.59	1877.31	9.30
Bisbenzoylacetonetetramethylenediiminocopper(II)	2.2736	5.609	1.14379	.3834	124.08	560.89	4.39
Bisbenzoylacetone-1,3-diimino-2-propanolocopper(II)	2.2721	7.655	1.14375	.5685	120.95	708.56	5.17
Bisbenzoylacetonepropylenediimino-oxovanadium(IV)	2.2731	8.722	1.14366	.3381	149.13	949.80	6.05
Bisdibenzoylmethanooxovanadium(IV)	2.2729	3.547	1.14387	.5572	171.47	497.76	3.61

atomic refraction to decrease with decreasing atomic number, as one might expect. The atomic refraction also seems to double in going from coördination number two to four (as in copper) which is analogous to the increase brought about by increasing the multiplicity of the bond. Approximately one-fourth of the atomic refraction in four-coördinated metals may therefore be ascribed to each single bond. The atomic refractions of cobalt and nickel are almost identical; four-coördinated vanadium should therefore be slightly smaller, say around 8 cc. with each bond contributing about 2 cc. In six-covalent vanadium the atomic refraction should approach 12 cc.

The total molar polarization of bisbenzoylacetonepropylene-diimino-oxovanadium(IV) is almost double that of the other three chelates of this ligand; also, the total molar polarization of bis-dibenzoylmethano-oxovanadium(IV) is unusually high. It seems most probable that this is the result of orientation polarization arising from the highly ionic character of the vanadium–oxygen bond perpendicular to the chelate rings. The oxygen atomic refraction therefore cannot be far from the O^- ion value of 7 cc.[11] Accordingly, a value of 6 cc. has been assigned to it in both vanadyl complexes. The total vanadyl group refraction is then taken as 18 cc.

While the uncertainty in the vanadyl group refraction value may be very great, the final dipole moment values should be quite reliable, since the former corresponds to only a very small percentage of the orientation polarization in both cases. For example, an error of ± 5 cc. in the vanadyl group refraction would produce an error of approximately ± 0.04 D. in the dipole moment of bisdibenzoylmethano-oxovanadium(IV) and ± 0.03 D. in that of bisbenzoylacetonepropylenediimino oxovanadium(IV).

Allowance has been made for the atomic polarization, since there is mounting evidence[12–16] in the case of metal chelate compounds that the atomic polarization makes an abnormally high contribution to the total polarization. In keeping with the assumptions of the previous work[3] the atomic polarization of all chelates containing trifluoroacetylacetone residues has been assigned a value of 50 ± 10% of P_E and those containing benzoylacetone or substituted benzoylacetone residues, a value of 35 ± 5% of P_E. The atomic polarization of the dibenzoylmethane vanadyl chelate should be similar to that of the benzoylacetone chelates, i.e. 35% of P_E; also, from polarization measurements made on the symmetrical bis-dibenzoylmethanopalladium (II) chelate the atomic polarization was found to be 36% of P_E.[17]

Results

For each of the nine metal chelates listed in Table I, dielectric constants (ϵ_{12}) and specific volumes (v_{12}) were measured for five or six solutions of varying concentration. As predicted by Halverstadt and Kumler[7] plots of these values against the weight

(11) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, Inc., New York, N. Y., 1955, p. 407.

(12) J. W. Smith and W. R. Angus, Proc. Roy. Soc. (London), 137A, 372 (1932).

(13) A. E. Finn, G. C. Hampson and L. E. Sutton, J. Chem. Soc., 1254 (1938).

(14) I. E. Coop and L. E. Sutton, ibid., 1269 (1938).

(15) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, 79, 4062 (1957).

(16) C. C. Meredith, L. Westland and G. F. Wright, ibid., 79, 2385 (1957).

(17) J. Mendelsohn and A. E. Martell, unpublished results.

fraction (w_2) of the solute yielded straight lines in all cases for concentrations less than 1%. In Table I are listed the parameters of these lines and all other values necessary for the calculation of the dipole moments found in the last column. As mentioned previously[5] these values are reproducible to ± 0.1 D.

Discussion

In the formation of Schiff bases from unsymmetrical diketones, such as trifluoroacetylacetone, p-bromobenzoylacetone, etc., two different conformations should be considered: one in which the polar groups (R) are adjacent to the diimine bridge (as in II), and the other in which these groups are in the terminal positions (as in I).
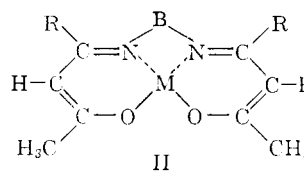
From a consideration of the dipole moments of the corresponding metal chelates, it is possible to ascertain the relative positions of such polar groups both in the chelates and in the ligands. In order to do this the dipole moment of each chelate listed in Table II has been calculated for the two possible planar configurations, with the assumption that the moments of the unsubstituted chelates investigated by McCarthy and Martell,[3] and the group moments of the substituents, are additive.

TABLE II

Chelate	Dipole moment (D.)		
	Est. struct. II	Est. struct. I	Obsd.
Bis-p-bromobenzoylacetone-propylenediiminocopper(II)	1.3	7.8	7.3
Bis-p-bromobenzoylacetone-propylenediiminonickel(II)	1.1	7.6	7.2
Bistrifluoroacetylacetone-propylenediiminocopper(II)	-0.4	9.5	9.7
Bistrifluoroacetylacetone propylenediiminonickel(II)	-0.6	9.3	9.3

The theoretical dipole moments were calculated from the values of the corresponding bisacetylacetonepropylenediimine metal chelates, together with the moments of benzotrifluoride[18] and bromobenzene.[19] Both lengths and bond angles in the two exterior chelate rings were assumed to be the

(18) P. Brown and T. DeVries, THIS JOURNAL, 73, 1811 (1951).

(19) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948, p. 28.

same as those of bis-salicylaldehyde-ethylenedi-iminocobalt(II) which were determined through X-ray diffraction measurements by Hughes, Barkelew and Calvin.[20] To illustrate the type of calculation by example: the theoretical dipole moment of bis - p - bromobenzoylacetonepropylenediiminocopper(II) corresponding to formula I equals that of bisacetylacetonepropylenediiminocopper(II) plus the difference between the components of the p-bromophenyl and methyl groups along the axis of symmetry

$$\mu = 4.63 + 2 \cos 34° (\mu_{p-bromophenyl} - \mu_{CH_3})$$

For the alternate formula II the difference between the components of the p-bromophenyl and methyl groups was subtracted, and the angle which these groups make with the axis of symmetry is approximately 32°.

As a first approximation the moment of p-bromophenyl group may be taken as that of bromobenzene (1.54 D.) minus one carbon–hydrogen bond moment. This value will include contributions due to resonance of the polar structures arising through charge shifts around the benzene ring; however, it will not take into account the effect of resonance with the chelate rings, which cannot be ascertained a priori.

It is seen that the dipole moment of toluene (0.4 D.) may be considered to be due to a methyl group moment minus a carbon–hydrogen bond moment. Therefore the replacement of a methyl group attached to a conjugated system by a p-bromophenyl group should give a dipole moment difference approximately equal to the vector difference between bromobenzene and toluene. This value then was added (or subtracted) vectorially to the previously determined moment of bisacetylacetonepropylene-diiminocopper(II) to obtain the predicted value of the p-bromobenzoyl derivatives.

In a similar manner the dipole moments of the bistrifluoroacetylacetonepropylenediimine metal chelates were calculated. The moment of benzotrifluoride, rather than that of trifluoromethane, was used in the latter cases because of the similarity in ionic resonance forms to be expected for benzotrifluoride and the conjugated metal chelate rings.

A consideration of the calculated and observed dipole moments in Table II shows that in both the bistrifluoroacetylacetone- and bis-p-bromobenzoyl-acetone-propylenediimine chelates the polar groups are located in the terminal position corresponding to formula I. The positions of the trifluoromethyl groups correspond with that observed previously[3] for bistrifluoroacetylacetone-ethylenediiminocopper(II).

It is interesting to also note that the dipole moment of bistrifluoroacetylacetonepropylenediimino-copper(II) is 0.13 D. higher than that of bistrifluo-roacetylacetone-ethylenediiminocopper(II). Similar small differences have been observed between the chelates of bisacetylacetonepropylenediimine and bisacetylacetone-ethylenediimine.[3] These effects have been attributed to an inductive electron release accompanying the substitution of a methyl

(20) E. Hughes, C. Barkelew and M. Calvin, OEMSr-279, March 15, 1944; also A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, New York, N. Y., 1952, p. 266ff.

group for a hydrogen atom in the diimine bridge. In Table II it may also be noted that the substitution of nickel for copper produces a lowering in the dipole moment; this is likewise in accord with the earlier results of McCarthy.[3]

The theoretical dipole moments of bistrifluoro-acetylacetonepropylenediimino-copper(II) and -nickel(II) corresponding to formula I are the same or possibly slightly lower than the observed moments. Lower values would in fact not seem unlikely in view of the possible ionic resonance forms in the conjugated metal chelate rings.
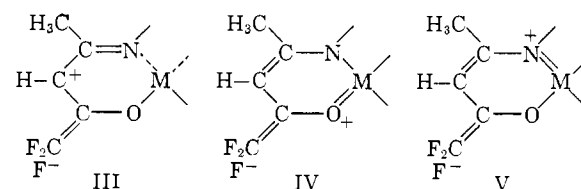
This exaltation in dipole moment as a result of resonance would be more apparent had the dipole moment of trifluoromethane (1.59 D.) been used in the calculation rather than benzotrifluoride (2.54 D.). The observed further increase in the dipole moment indicates that the metal chelate ring is somewhat more polarizable than the benzene ring.

The observed dipole moments of bis-p-bromo-benzoylacetonepropylenediimino-copper(II) and -nickel(II) are respectively 0.5 and 0.4 Debye unit less than the theoretical values calculated on the basis of formula I. This difference is in accord with the postulated ionic forms of the chelates shown in VI and VII. The bromobenzene moment was used to calculate the theoretical values, which should consequently include resonance effects within the p-bromophenyl groups.
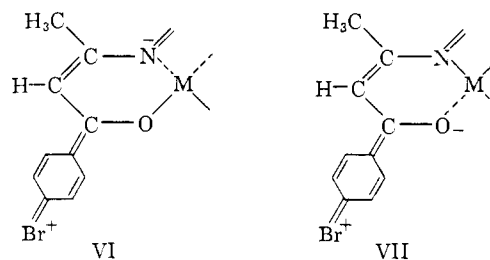
The differences between the observed and calculated values are thus a reflection of the resonance interaction between the p-bromophenyl groups and the chelate ring system.

The dipole moment of bis-m-nitrobenzoylace-tonepropylenediiminonickel(II) is 9.43 D., or 5 Debye units higher than the corrrsponding unsubstituted nickel(II) chelate. The two nitro group moments must, therefore, be acting in the same general direction as the resultant of the metal-donor bonds. This correlation must mean that the m-nitrophenyl groups are in the terminal positions in bis-m-nitrobenzoylacetonepropylenediimine and its metal chelates. Unlike the p-bromophenyl derivatives rotation of the m-nitrophenyl groups results in various orientations of the principal moments in the chelate molecule, the average of which gives the observed moment. Because of the varia-

tion of moment with rotation of the phenyl rings, and the fact that the rotations of the substituent groups undoubtedly are restricted, no attempt was made to calculate a theoretical dipole moment for the nitro compound.
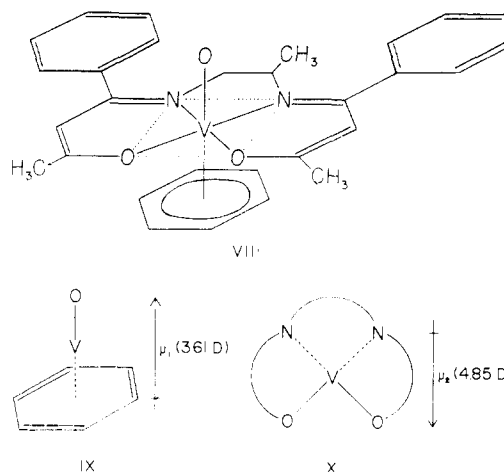
The copper(II) chelate of bisbenzoylacetonetetramethylenediimine has a seven-membered central chelate ring. As a first approximation one would expect the dipole moment of this molecule to be slightly less than that of bisacetylacetone-ethylenediiminocopper(II) (μ = 4.53 D.) and about the same as that of bisbenzoylacetonetrimethylenediiminocopper(II) (μ = 4.24 D.) as a result of the strain in the ethylene bridge which gives a N–Cu–N angle which is somewhat less than 90°. The observed moment is actually only slightly lower than that of the ethylene compound and 0.15 D. higher than the trimethylene derivative. It would seem that in addition to the dipole moment lowering effect brought about by increasing the N–Cu–N angle, there is also an exaltation in the polarity of the molecule as the result of further increasing the size of the bridge from two or three to four methylene groups.

After recrystallization from benzene the vanadyl chelates of dibenzoylmethane and bisbenzoylacetonepropylenediimine were each found to be solvated with one molecule of benzene. Accordingly, the total molar polarizations of both vanadyl complexes were calculated on the basis of the solvated form, VIII, since the measurements were made in benzene.

The dipole moment of bisdibenzoylmethano-oxovanadium(IV) is in reality the benzene-vanadyl group moment with the direction of the vector as indicated in IX. Other polar bonds in the molecule are arranged symmetrically giving rise to a net zero moment.

If it is assumed that the moment of the group represented by IX has the same value in both vanadyl chelates, the observed dipole moment of bisbenzoylacetonepropylenediimino-oxovanadium(IV) (μ_3) has rectilinear components μ_1 and μ_2 (the resultant moment of the nearly coplanar vanadium chelate rings), since μ_1 and μ_2 are nearly perpendicular to each other. We therefore have the relationship: $\mu_3{}^2 = \mu_1{}^2 + \mu_2{}^2$, from which it is possible to calculate the dipole moment due to the vanadium chelate rings. This particular value is of interest for com-

parison with the dipole moments of the other three metal chelates of bisbenzoylacetonepropylenediimine, already determined.[3]

The value of 4.85 D. calculated for the component of the coplanar chelate rings in bisbenzoylacetonepropylenediimino-oxovanadium(IV) is greater than the observed dipole moments of bisbenzoylacetonepropylenediimino-copper(II) (4.54 D.), -nickel(II) (4.35 D.) and -cobalt(II) (4.03 D.). As mentioned previously[3] the influence of the metal atom on the dipole moment can be related to the stability (or homopolarity of the metal-donor bond) and the basicity of the metals (which in turn is related to the sum of the first and second ionization potentials). From the few equilibrium constants that are available,[21] it appears that the stabilities of vanadyl chelates are very close to those of the corresponding copper chelates. On the other hand the sum of the first and second ionization potentials of vanadium (20.9 ev.)[22] is considerably less than that of either copper, nickel or cobalt. This should make the V–O chelate bonds more ionic than the other metal–oxygen chelate bonds. These factors may therefore account for the high value of 4.85 D

(21) J. Bjerrum, G. Schwarzenbach and L. Sillen, "Stability Constants," Part I, Organic Ligands, The Chemical Society (London) Burlington House, W. T., 1957.

(22) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952. p. 157.