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# Dipole Moments of Metal Chelate Compounds. II. Metal Chelates of Analogs of Bisacetylacetone-ethylenediimine[1,2]

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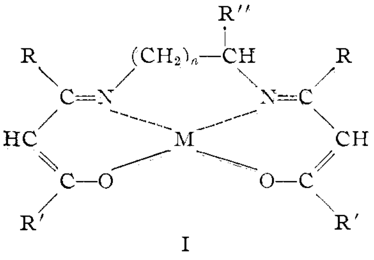
RECEIVED DECEMBER 15, 1955

The electric dipole moments of twelve metal chelates of analogs of bisacetylacetone-ethylenediimine were determined; the metals used were palladium, copper, nickel and cobalt. All the compounds are four-coördinated and have a square planar configuration. The order of decreasing dipole moment, Pd > Cu > Ni > Co, was found to parallel decreasing chelate stability. The high electric dipole moment of bistrifluoroacetylacetonocopper(II) indicates that the compound is about 60% in the *cis* form. Its magnetic moment seems to confirm the expected square planar configuration.

## Introduction

The use of electric dipole moment measurements as an aid in elucidating the structure of metal chelate compounds has been somewhat neglected. Wesson[3] lists the moments for only 33 metal chelates. Since 1948, Draney and Cefola[4] and Milone and Borello[5] have published values for several nickel chelates, and Richmond and Freiser[6] have measured the moments of mono- and diacetylferrocene.

The present investigation was undertaken to determine what effect (1) a change of the metal atom, and (2) structural changes in the ligand, have on the dipole moment of a metal chelate. For this purpose, metal chelates of analogs of bisacetylacetone-ethylenediimine were used. They are listed in Table I and shown diagrammatically in formula I. In chelates containing (a) an acetylacetone residue, $R = R' = CH_3$; (b) a benzoylacetone residue, $R = C_6H_5$, $R' = CH_3$; (c) a trifluoroacetylacetone residue, $R = CH_3$, $R' = CF_3$. Where the bridge is (a) ethylenediamine, $n = 1$, $R'' = H$; (b) propylenediamine, $n = 1$, $R'' = CH_3$; (c) trimethylenediamine, $n = 2$, $R'' = H$. In addition to the compounds represented by I, bistrifluoroacetylacetonocopper(II) also was employed. The dipole moments of the ligands together with a discussion of their structure have been given in a previous publication.[7]



I

## Experimental

**Procedure.**—The preparation and purification of the compounds used in this investigation were outlined in a previous publication.[8] The method of measuring the dielectric constants and a description of the cell and heterodyne oscillator used have also been described.[7] Solution densities were determined by means of a 25-ml. Rieschauer pycnometer. Benzene, the solvent used in all measurements, was purified by standard procedures. All measurements were made in an oil-bath maintained at 25.25 ± 0.02°; at this temperature the dielectric constant and specific volume of benzene are 2.2722[9] and 1.14541,[10] respectively.

**Calculations.**—The molar polarization of the solute at infinite dilution ($P_{2\infty}$) was determined by the method of Halverstadt and Kumler.[11] Plots of the dielectric constants ($\epsilon_{12}$) and specific volumes ($v_{12}$) of the solutions against the weight fractions ($w_2$) of the solute were found in all cases to be linear for $w_2 \leqq 0.01$. The values of the intercepts were in most cases very close to the values of the dielectric constant and specific volume of pure benzene. $P_{2\infty}$ was calculated by means of the equation

$$P_{2\infty} = \frac{3\alpha v_1 M_2}{(\epsilon_1 + 2)^2} + M_2(v_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

where $\alpha$ and $\epsilon_1$ are the slope and intercept of the plot of $\epsilon_{12}$ against $w_2$, $\beta$ and $v_1$ are the slope and intercept of the plot of $v_{12}$ against $w_2$, and $M_2$ is the molecular weight of the solute. The parameters of all straight lines were calculated by the method of least squares.

For the conditions employed, the dipole moment, $\mu$, is equal to $0.01281\sqrt{P_0T}$, where $T$ is the absolute temperature, and $P_0$, the orientation polarization, is evaluated by subtracting $P_E$, the electron polarization, and $P_A$, the atom polarization, from $P_{2\infty}$.

**Determination of $P_E$.**—Since all the chelates used are highly colored, the electron polarizations were determined by summation of the bond refractivities. The table of Vogel[12] was used in determining the sum for all bonds except the four to the metal atom. To each of the sums thus calculated was added the refractivity of the proper metal atom. The values used for the latter are: nickel, 10.0 cc.; cobalt, 10.5 cc.; copper, 14.5 cc.; palladium, 16.8 cc. The value for copper is the average of values derived from (1) the data of Sutton and co-workers[13] for the electron polarization of bisacetylacetonocopper(II), and (2) the application of the Lorenz–Lorentz equation to crystallographic data for various copper compounds. The values for nickel and cobalt were estimated from crystallographic data alone, while the value for palladium was derived from the electron polarizations of three palladium complexes given by Mann and Purdie.[14] The metal refractivity values are admittedly only approximations; in the calculation of errors, however, they were assumed to be accurate to ±25%.

**Determination of $P_A$.**—From data of Sutton and co-workers[13,15] for $P_{2\infty}$ and $P_E$ of several metal acetylaceton-

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[1] Abstracted from the dissertation submitted by P. J. McCarthy in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Clark University, 1955.

[2] This work was sponsored by the Research Corporation and by the Office of Ordnance Research under Contract #DA-19-020-ORD-3243.

[3] L. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948.

[4] J. J. Draney, Jr., and M. Cefola, THIS JOURNAL, **76**, 1975 (1954).

[5] M. Milone and E. Borello, *Ann. chim. appl.*, **41**, 320 (1951).

[6] H. Richmond and H. Freiser, THIS JOURNAL, **77**, 2022 (1955).

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

[8] P. J. McCarthy, K. Ueno, R. J. Hovey and A. E. Martell, *ibid.*, **77**, 5820 (1955).

[9] L. Hartshorn and D. Oliver, *Proc. Roy. Soc. (London)*, **A123**, 664 (1929).

[10] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N.Y., 1946, p. 25.

[11] I. Halverstadt and W. Kumler, THIS JOURNAL, **64**, 2988 (1942).

[12] A. Vogel, *Chemistry and Industry*, 358 (1950).

[13] A. Finn, G. Hampson and L. Sutton, *J. Chem. Soc.*, 1254 (1938).

[14] F. Mann and D. Purdie, *ibid.*, 1549 (1935).

[15] I. Coop and L. Sutton, *ibid.*, 1269 (1938).

TABLE I

| | Compound | $\epsilon_1$ | $\alpha$ | $v_1$ | $-\beta$ | $P_E$ (cc.) | $P_{2\infty}$ (cc.) | $\mu(D)$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Bisacetylacetone-ethylenediiminocopper(II) | 2.2712 | 8.794 | 1.14534 | 0.4466 | 75.8 | 532.9 | 4.53 |
| 2 | Bisacetylacetone-ethylenediiminonickel(II) | 2.2729 | 7.969 | 1.14492 | .4047 | 71.3 | 483.2 | 4.29 |
| 3 | Bisacetylacetone-ethylenediiminopalladium(II) | 2.2725 | 8.312 | 1.14544 | .5588 | 78.1 | 572.2 | 4.72 |
| 4 | Bisacetylacetone-propylenediiminocopper(II) | 2.2711 | 8.723 | 1.14528 | .4006 | 80.4 | 559.1 | 4.63 |
| 5 | Bisacetylacetone-propylenediiminonickel(II) | 2.2705 | 8.103 | 1.14544 | .4113 | 76.0 | 514.8 | 4.43 |
| 6 | Bisacetylacetonetrimethylenediiminocopper(II) | 2.2708 | 7.451 | 1.14535 | .4158 | 80.4 | 486.0 | 4.23 |
| 7 | Bistrifluoroacetylacetone-ethylenediiminocopper(II) | 2.2714 | 25.975 | 1.14535 | .5873 | 74.4 | 1991.8 | 9.60 |
| 8 | Bistrifluoroacetylacetonocopper(II) | 2.2713 | 3.076 | 1.14528 | .4961 | 62.8 | 285.6 | 3.06 |
| 9 | Bisbenzoylacetonepropylenediiminocopper(II) | 2.2747 | 6.144 | 1.14533 | .4143 | 119.4 | 582.3 | 4.54 |
| 10 | Bisbenzoylacetonepropylenediiminonickel(II) | 2.2723 | 5.672 | 1.14527 | .3908 | 114.9 | 541.6 | 4.35 |
| 11 | Bisbenzoylacetonepropylenediiminocobalt(II) | 2.2738 | 5.004 | 1.14538 | .3998 | 115.4 | 488.0 | 4.03 |
| 12 | Bisbenzoylacetonetrimethylenediiminocopper(II) | 2.2725 | 5.413 | 1.14532 | .3843 | 119.4 | 528.1 | 4.24 |

ates in benzene solution (8 values) and in the gas phase (5 values), it was calculated that $P_A = 50 \pm 10\% \, P_E$. Since the compounds investigated in this research have a structure similar to that of the metal acetylacetonates, the above value was used for the atom polarization of all the chelates except those having the benzoylacetone bridged structure.

In this research bisbenzoylacetonocopper(II) was found to have a molar polarization of 139.7 cc. $P_E$ was estimated as described above; with the assumption that $P_0 = 0$, $P_A$ was found to be 36.6 cc., or 35% $P_E$. The value, $P_A = (35 \pm 5)\% \, P_E$, was accordingly used for all chelates having the benzoylacetone bridged structure. The limitations of these approximations are clear, but they were employed because more accurate data are not available.

## Results

Table I contains the parameters calculated from the experimental data gathered for the twelve compounds. In each case 4 or 5 solutions were measured. Values for $P_E$, $P_{2\infty}$ and $\mu$ were determined as outlined above. The values in all cases are believed to be accurate to about $\pm 0.1$ $D$. The errors result principally from uncertainties in $P_E$ and $P_A$, for the uncertainty in the value of $P_{2\infty}$ is negligible in comparison with these two.

## Discussion

**Spatial Arrangement of Metal Bonds.**—The analyses of the compounds indicate that none of them has more than four groups in its coördination sphere. The nature of the ligands used in preparing the chelates (except #8) makes the formation of tetrahedral complexes sterically very improbable, if not impossible. A square planar configuration may therefore be safely ascribed to all the compounds listed in Table I (except possibly to #8). This conforms with the usual structure of copper(II), palladium(II) and cobalt(II) four-coördinated complexes. The square planar structure for the nickel(II) chelates was confirmed by magnetic susceptibility measurements. Bisacetylacetone-ethylenediiminonickel(II) has been shown to be diamagnetic both in chloroform and ethanol solutions,[16] as well as in the solid state.[17] Bisacetylacetonepropylenediiminonickel(II) and bisbenzoylacetone-ethylenediiminonickel(II) were measured and also found to be diamagnetic. Because of these data, a square planar structure can be ascribed to all the nickel chelates in Table I.

**Dipole Moment and Stability.**—Jensen[18] has found the dipole moments of $\alpha$-$(PtCl_2(Et_2S)_2)$ and $\alpha$-$(PdCl_2(Et_2S)_2)$ to be 2.41 and 2.19 $D$, respectively. Combining these values with the data in Table I, it is concluded that the order of decreasing dipole moment for a series of chelates of metals of similar bond hybridization with a single ligand is Pt > Pd > Cu > Ni > Co. The order for these square planar complexes is identical with the order of stability found for metal acetylacetonates and some other chelates by Mellor and Maley.[19] This parallel order would be difficult to predict *a priori*, since two opposing forces are here at work. First, it is clear that the most stable chelates are formed by the metals which form the strongest homopolar bonds.[20] The stronger the homopolar bond (in this case, especially the nitrogen–metal bond), the more closely is the donated electron pair held by the metal, and the greater the effective positive charge increase on the nitrogen atom. This might be expected to cause an increase in the electric moment of the whole molecule as one proceeds from Co through Ni, Cu and Pd to Pt. This is the result actually found. However, counteracting this effect is that caused by the decreasing ionic character of the metal–oxygen bond with decreasing basicity of the metal atom. The order of basicity of the metals used can be determined by considering the sum of the first and second ionization potentials of these metals. The sums (in e.v.) for which data are available are[21]: Cu, 28.02; Pd, 27.8; Ni, 25.85; Co, 25.15. Copper is the most electrophilic, and therefore the least basic. Because of this, the copper–oxygen bond will, for example, be less ionic than the cobalt–oxygen bond in corresponding chelates. The copper–oxygen bond would then be expected to have a smaller moment than the more ionic cobalt–oxygen bond. Since this effect acts in opposition to that due to the homopolarity of the metal–nitrogen bond, we must conclude from the experimental data that the metal–nitrogen bond moment changes more considerably with the nature of the metal than does the metal–oxygen bond moment.

**Bond Lengths and Angles.**—The parameters of bissalicylaldehyde-ethylenediiminocobalt(II), as determined by X-ray diffraction by Hughes, Barkelew and Calvin,[22] are shown in Fig. 1. Because of

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[16] J. Willis and D. Mellor, THIS JOURNAL, **69**, 1237 (1947).

[17] N. Hall and B. Willeford, *ibid.*, **73**, 5419 (1951).

[18] K. A. Jensen, *Z. anorg. allgem. Chem.*, **225**, 97 (1935).

[19] D. Mellor and L. Maley, *Australian J. Sci. Research*, **2A**, 92 (1949).

[20] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952, p. 185.

[21] W. Latimer, "Oxidation Potentials," Prentice–Hall, Inc., New York, N. Y., 2nd Edition, 1952, pp. 15 f.

[22] E. Hughes, C. Barkelew and M. Calvin, quoted in ref. 20, pp. 266 ff.

the similarity between this compound and those used in this investigation, we may assume these parameters are close approximations to those of bisbenzoylacetonepropylenediiminocobalt(II). However, the two carbon–carbon bonds (1.42 and 1.39 Å.) are in bissalicylaldehyde-ethylenediiminocobalt(II) largely single and aromatic, respectively, while the corresponding bonds in bisbenzoylacetonepropylenediiminocobalt(II) are largely single and double, respectively. One would therefore expect these bond lengths to be slightly different from those given. The angles in the six-membered rings would also of necessity change slightly.

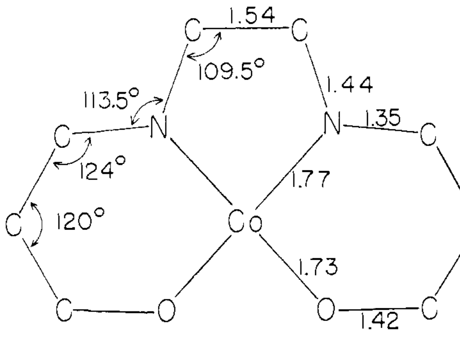


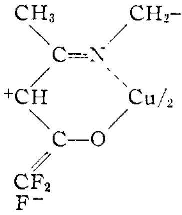
Fig. 1.—Bond angles and distances in bisacetylacetone-ethylenediimino-Co(II).

The substitution of copper or nickel for cobalt should change the molecular parameters only slightly, if we may judge from the covalent radii of these elements[23]: Cu, 1.173 Å.; Ni, 1.149 Å.; Co, 1.157 Å. One might expect a greater change for the palladium complex, since the covalent radius of palladium is 1.278 Å. The nature and extent of this change are, however, impossible to predict.

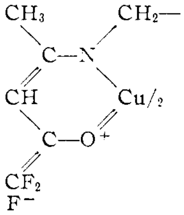
The difference in the moments of bisacetylacetone-ethylenediiminocopper(II) and the corresponding trimethylene compound can be ascribed in part to the difference in the N–Cu–N angle. Were this the only change in the molecule, an increase of about 7° in this angle in the trimethylene compound would cause the decrease in $\mu$ observed. Some increase in bond angle in this compound is rendered plausible by the electrical repulsion of the large positive formal charges on the two nitrogen atoms. The longer chain of the trimethylene bridge allows the two nitrogen atoms to be further separated with a consequent decrease in repulsion energy. In one or both of these compounds then, the N–Cu–N angle must not be equal to 90°. This is not unusual, for, in some cases where strain exists, the bond angles have been found to differ from the expected values; several examples are reviewed by Martell and Calvin.[24]

The slight increase in moment observed when the propylene group is substituted for the ethylene group in the bridge may be due to contributions from ionic resonance forms involving the asymmetric methyl in the propylene group, and to the inductive effect of this electron-releasing methyl group.

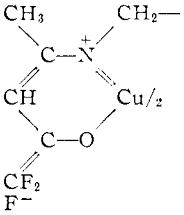
The high moment of bistrifluoroacetylacetone-ethylenediiminocopper(II) shows that the $-CF_3$ groups must be in the position assigned to them in formula I. If the bond angles in this molecule are the same as those given in Fig. 1, and if the methyl group moment is taken to be 0.4 *D* (based on $\mu_{C^- - H^+} = 0.4\ D$), the moment of the $-CF_3$ group is calculated to be 2.66 *D*. This value agrees with that which Brown and DeVries[25] derived from a study of benzotrifluoride (*viz.*, 2.54 *D*). As in benzotrifluoride, so in the compound under discussion, the high moment of the $-CF_3$ group may be considered to be due to the ionic resonance forms which contribute to the structure of the molecule. Some of these are shown in formulas IIa-c.



IIa

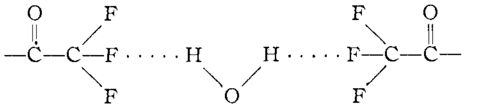


IIb



IIc

Bistrifluoroacetylacetonocopper(II) was expected to be non-polar in view of the tendency of copper(II) to form planar *trans* complexes. The observed moment, 3.06 *D*, indicates that the compound is at least partially in the *cis* form. If the molecular parameters are similar to those shown in Fig. 1, and if the $-CF_3$ group moment is taken to be 2.66 *D*, the square planar compound would be about 60% in the *cis* configuration. A possible explanation is the following: since the chelate compound was prepared in aqueous solution, two ligand molecules could easily be joined by hydrogen bonds to a single water molecule as shown in formula III. The two ligand molecules would then be pre-arranged



III

to form the *cis* configuration, and chelation with a metal atom would produce a high percentage of the *cis* isomer. It is not clear, however, why the effect is not more complete than the data indicate. According to the criterion of Ray and Sen,[26] the measured magnetic moment of the compound (1.83 B.M.) seems to indicate that the expected square planar configuration actually obtains. A definitive assignation of structure must, however, await further evidence.

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[23] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 135.

[24] Ref. 20, pp. 175 ff., 318 ff.

[25] P. Brown and T. DeVries, THIS JOURNAL, **73**, 1811 (1951).

[26] P. Ray and D. Sen, *J. Indian Chem. Soc.*, **25**, 473 (1948).