Inorganica Chimica Acta, 48 (1981) 33–36
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Dipole Moments of some Metal Complexes of Six New Monothio-β-Diketones containing Perfluoroalkyl Group

MANORANJAN DAS

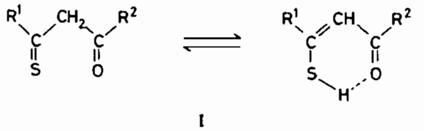
School of Chemistry, The University of New South Wales, Kensington, N.S.W., 2033, Australia

Received August 14, 1980

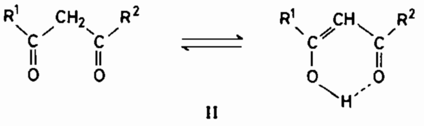
Dipole moments of nickel(II), palladium(II) and cobalt(III) complexes of six new monothio-β-diketones $R^1C(SH) = CHCOR^2$ *(*R^1 *= phenyl, 2'-naphthyl and 2'-thienyl;* $R^2 = C_2F_5$ *and* $CF_2CF_2CF_3$*) were determined by static-polarization measurements. With same* R^2 *the dipole moments varies when* R^1 *arranged as 2'-thienyl > 2'-naphthyl > phenyl. With same* R^1 *the dipole moments varies as* $C_3F_7 > C_2F_5$*. The latter values are small: 0.03–0.37 D for the nickel, 0.08–0.24 D for the palladium and 0.12–0.16 D for the cobalt complexes. Nickel(II) and palladium(II) complexes definitely have* cis-square-planar *structures. Cobalt(III) complexes perhaps have* facial-octahedral *configurations.*

Introduction

In the last few years we have reported the dipole moments of some transition metal complexes of a large number of trifluoromethyl monothio-β-diketones (I; $R^2 = CF_3$). The solubilities in organic solvents and the monomeric nature of these complexes make it possible to determine their dipole moments in benzene solutions. In the course of these studies we have investigated the effect of substituents, both electrophilic and nucleophilic, in the phenyl ring of $PhC(SH) = CHCOCF_3$ on the dipole moment of their metal complexes [1–6]. The dipole moments a few metal complexes of difluoromethyl monothio-β-diketones (I; $R^2 = CHF_2$, $R^1 = C_6H_5$, p-$CH_3C_6H_4$ and 2'-thienyl) were reported by us [7].



I



II

Belcher *et al.* for the first time prepared [8] monothio derivatives of pentafluoro- and heptafluoroalkyl β-diketones [II; $R^1 = (CH_3)_3C$, $R^2 = C_2F_5$ and $CF_2CF_2CF_3$]. They could not isolate these perfluoro monothio-β-diketones in pure state and used the impure products for the preparation of their nickel complexes. However, Sweet *et al.* prepared this two monothio compounds in pure state. The position of sulphur atom in the pentafluoro compound was established by mass spectra [9, 10].

Now we have prepared six new monothio-β-diketones, $RC(SH) = CHCOC_2F_5$ and $RC(SH) = CHCOCF_2CF_2CF_3$, with R = phenyl, 2'-naphthyl and 2'-thienyl. The dipole moments of nickel(II), palladium(II) and cobalt(III) complexes of these monothio-β-diketones are discussed in this report.

Experimental

Preparation of the β-Diketones

The β-diketones were prepared by Claisen condensation of methyl ketone (R^1COCH_3) and ethyl perfluorocarboxylates ($CF_3CF_2COOC_2H_5$ and $CF_3CF_2CF_2COOC_2H_5$), catalyzed by sodium methoxide [6].

1,1,1,2,2-Pentafluoro-5-phenyl-3,5-pentanedione (II; R^1 = phenyl, $R^2 = C_2F_5$), b.p. 226 °C (*Anal.* Found: C, 49.26; H, 2.63. Calc. for $C_{11}H_7F_5O_2$: C, 49.62; H, 2.65%).

1,1,1,2,2-Pentafluoro-5-(2'-naphthyl)-3,5-pentanedione (II; R^1 = 2'-naphthyl, $R^2 = C_2F_5$), m.p. 36 °C (*Anal.* Found: C, 56.90; H, 2.98. Calc. for $C_{15}H_9F_5O_2$: C, 56.99; H, 2.87%).

1,1,1,2,2-Pentafluoro-5-(2'-thienyl)-3,5-pentanedione (II; R^1 = 2'-thienyl, $R^2 = C_2F_5$), b.p. 231 °C (*Anal.* Found: C, 39.81; H, 2.01. Calc. for $C_9H_5F_5O_2S$: C, 39.71; H, 1.85%).

1,1,1,2,2,3,3-Heptafluoro-6-phenyl-4,6-hexanedione (II; R^1 = phenyl, $R^2 = CF_3CF_2CF_2$), b.p. 234 °C (*Anal.* Found; C, 46.02; H, 2.12. Calc. for $C_{12}H_7F_7O_2$: C, 45.57; H, 2.23%).

1,1,1,2,2,3,3-Heptafluoro-6-(2'-naphthyl)-4,6-hexanedione (II; R^1 = 2'-naphthyl, $R^2 = CF_3CF_2CF_2$), m.p. 31 °C (*Anal.* Found: C, 52.15; H, 2.35. Calc. for $C_{16}H_9F_7O_2$: C, 52.48; H, 2.48%).

1,1,1,2,2,3,3-Heptafluoro-6-(2′-thienyl)-4,6-hexanedione* (II; R^1 = 2′-thienyl, R^2 = $CF_3CF_2CF_2$), b.p. 241 °C (*Anal.* Found: C, 37.17; H, 1.59. Calc. for $C_{10}H_5F_7O_2S$: C, 37.27; H, 1.56%).

The molecular weight of these β-diketones were determined by EI mass spectra.

Preparation of the Monothio-β-diketones

A solution of 5 g β-diketone in 250 ml absolute alcohol taken in a two necked one litre round bottom flask and cooled in an alcohol–dry ice bath. Dry hydrogen sulphide was passed for 30 min. followed by dry hydrogen chloride for 15 min. The mixture was allowed to stand at room temperature for about 20 h. The flask was fitted with a calcium chloride drying tube to prevent access of moisture. The mixture was cooled again to –70 °C and the passage of gases were repeated. The mixture was then allowed to stand at room temperature for about 20 h. The red solution was poured to 400 g ice–water mixture and the mixture was kept in an ice bath for 30 min. The monothio-β-diketone was extracted with 75 ml petroleum ether (b.p. 40°–60 °C). After drying over anhydrous sodium sulphate, the solvent was evaporated off to get the ligand as red oil. No attempts were made to purify the products. The impure products were used for the preparation of their metal complexes.

Preparation of the Complexes

Nickel(II)

Nickel(II) acetate tetrahydrate (1.5 g, 6 mmol) in warm alcohol (100 ml) was added to a solution of the monothio-β-diketone (12 mmol + 1 g) in alcohol (30 ml). The mixture was cooled in ice and the resulting brown precipitate filtered off. The products were recrystallized twice from acetone–petroleum ether mixture. Due to high solubility the products with R^1 = 2′-thienyl were recrystallized once only.

Palladium(II)

A filtered solution of potassium tetrachloropalladate(II) (2.5 g, 7.7 mmol) in water (75 ml) was added to a solution of the monothio-β-diketone (15.5 mmol + 1 g) in acetone (75 ml). The resulting precipitate was recrystallized twice from acetone. The products with R^1 = 2′-thienyl were recrystallized only once.

Cobalt(III)

Cobalt(II) acetate tetrahydrate (1 g, 4 mmol) in ethanol (150 ml) was added to a solution of the monothio-β-diketone (12 mmol + 1.5 g) in ethanol (50 ml). The brown solution was filtered and air passed through the solution for four hours. The brown deposit was filtered and washed with ethanol. When R^1 = C_6H_5, no solid was formed after the passage of air. The solution was evaporated to 75 ml and cooled. To this solution 5 ml water was added and the mixture was kept overnight in the refrigerator. The solid was filtered and washed with ice cooled 90% alcohol.

Analytical data for the complexes are shown in Table I.

Determination of the Dipole Moments

Dielectric constants were measured at 25 °C with a WTW Dipolemeter Type DM 01 with DFL-1 cell. Refractive indices were obtained at 25 °C with an Abbe 60 Refractometer. The detailed procedure of the calculation of the dipole moments was described in our earlier report [6].

Results and Discussion

The oxygen atom of the β-diketones which is further from the electronegative C_2F_5 and C_3F_7 groups were replaced by a sulphur atom during the preparation of the monothio-β-diketones. This has been proved by the presence of R^1CS in the EI mass spectra of the palladium complexes.

The rate of conversion of fluorinated β-diketones to their monothio derivatives decreases as the number of fluorine atoms in R^2 increases *i.e.*, $CHF_2 > CF_3 > C_2F_5 > C_3F_7$. This was evident from the rate of the development of red colour of the monothio compounds after H_2S and HCl gases were passed through the alcoholic solutions of β-diketones, and required to pass the gases twice when R^2 = C_2F_5 and C_3F_7. It has been suggested that the percentage of enolic form of β-diketone increases with increasing fluorination of R^2. The reaction of H_2S with β-diketones occurs when the latter are in keto form and the function of HCl, by increasing to polarity of the solvent, shifts the keto–enol tautomeric equilibrium toward the keto form [12].

Dipole moments of the metal complexes of the monothio-β-diketones were determined by the static-polarization measurements and the values are given in Table II together with the moments previously reported for the related metal complexes. The latter values are shown for the purposes of comparison. Metal chelates often have an appreciable value for atomic polarization [13, 14]. This is due to the vibration of the chelate rings with respect to the rest of the molecule and its value increases with the increasing number of chelate rings. Dipole moment determined by the static-polarization method include the contribution due to this effect. Our earlier results [1, 3] indicate that the average values for atomic

---

*The compound is listed in Eastman Organic Chemicals (USA) Catalog No. 47 (1974).

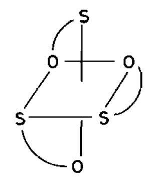
TABLE I. Analytical Data for the Complexes of $R^1C(SH) = CHCOR^2$.

R^1	R^2	Compound	M.p. °C	% Found				% Calcd.			
				C	H	Metal	S	C	H	Metal	S
Phenyl	C_2F_5	NiL_2	148	42.52	1.69	9.57	9.98	42.53	1.95	9.45	10.32
		PdL_2	152	39.48	1.62	15.99	9.41	39.50	1.81	15.91	9.59
		CoL_3	97	44.16	1.91	6.57	10.46	43.92	2.01	6.53	10.66
2′-Naphthyl	C_2F_5	NiL_2	193	49.78	2.11	8.26	8.65	49.97	2.24	8.14	8.89
		PdL_2	203	46.83	2.29	13.86	8.36	46.86	2.09	13.84	8.34
		CoL_3	209	51.43	2.18	5.47	9.06	51.36	2.30	5.60	9.14
2′-Thienyl	C_2F_5	NiL_2	184	34.16	1.42	9.35	19.88	35.15	1.27	9.27	20.25
		PdL_2	210	32.04	1.11	15.64	19.11	31.76	1.18	15.63	18.83
		CoL_3	231	35.09	1.19	6.30	20.87	35.23	1.31	6.40	20.90
Phenyl	C_3F_7	NiL_2	125	39.91	1.77	8.11	8.96	39.98	1.68	8.14	8.89
		PdL_2	138	37.24	1.53	13.72	8.64	37.50	1.57	13.84	8.34
		CoL_3	103	40.81	1.58	5.67	9.37	41.09	1.72	5.60	9.14
2′-Naphthyl	C_3F_7	NiL_2	181	46.78	1.95	7.15	7.67	46.82	1.96	7.15	7.81
		PdL_2	164	44.33	1.94	12.10	7.43	44.25	1.86	12.25	7.38
		CoL_3	202	47.48	2.01	4.79	7.65	47.95	2.01	4.90	8.00
2′-Thienyl	C_3F_7	NiL_2	162	33.02	1.03	7.98	16.90	32.77	1.10	8.01	17.49
		PdL_2	179	30.37	1.10	13.53	16.38	30.76	1.03	13.63	16.43
		CoL_3	217	33.53	1.07	5.41	17.81	33.65	1.13	5.50	17.96

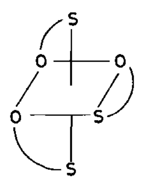
TABLE II. Dipole Moments of the Metal Complexes of $R^1C(SH) = CHCOR^2$.

R^1		R^2			
		C_3F_7	C_2F_5	CF_3	CHF_2
Phenyl	NiL_2	5.38	5.35	4.92^a	3.27^c
	PdL_2	5.63	5.55	5.02^a	
	CoL_3	6.68	6.54	6.54^a	
2′-Naphthyl	NiL_2	6.07	5.86	5.47^b	
	PdL_2	6.24	6.00	5.55^b	
	CoL_3	7.36	7.20	6.90^d	
2′-Thienyl	NiL_2	6.31	5.94	5.74^a	3.87^c
	PdL_2	6.38	6.18	5.88^a	
	CoL_3	7.60	7.48	7.14^a	4.95^c

[a] Reference 1. [b] Reference 4. [c] Reference 7. [d] Reference 11.



Facial



Meridional

polarization are 0.32 and 0.85 Debye for the square-planar and octahedral metal chelates of monothio-β-diketones, respectively. No corrections were applied for the compounds in Table II.

The unsymmetrical bidentate ligands such as monothio-β-diketones can form either *cis* or *trans* in square-planar, and *facial* or *meridional* configurations in octahedral complexes.

The high dipole moments of nickel(II) and palladium(II) complexes definitely indicate their *cis*-square-planar configurations. Preferential formation of *cis*- structure in the transition metal complexes of sulphur containing ligands is probably due to d_π–d_π bonding between the metal and sulphur atoms [15]. The electron filled d orbitals of transition metal acts as a donor and the vacant d orbitals of sulphur atoms act as an acceptor. For such bonding the sulphur–metal–sulphur angle must be about 90°, resulting *cis* structures for NiL_2 and PdL_2. An alternate explanation for the *cis* structure is that it may be due to the weak nonbonded S···S interaction [16]. X-ray structure determinations have confirmed the configuration for nickel [16–18] and palladium [19] complexes of some monothio-β-diketones. Such *cis* structures were also found in the nickel complexes of sulphur containing bidentate Schiff bases [20]. For a given monothio-β-diketone PdL_2 has slightly higher moment than NiL_2. It is interesting to note that palladium has higher *b* class character than nickel [21].

It is not possible from the experimental dipole moments of CoL_3 to distinguish between the *facial*- and *meridional*-octahedral configurations. However, relatively high values indicate the probability of their *facial* configuration. Three sulphur atoms in the *facial* structure are at right angles to the metal and thus in correct position for d_π–d_π bonding with the metal atom. X-ray studies of some iron(III) and cobalt(III) complexes of monothio-β-diketones show their *facial* structures [22, 23]. The ^1H NMR studies by Holm *et al.* also showed the *facial* structure of some tris(monothio-β-diketonato)cobalt(III) [24]. Recently we have reported [25] ^{13}C and ^{19}F NMR spectra of some metal complexes of $RC(SH) = CHCOCF_3$. The spectra of CoL_3 complexes showed single resonance for the CF_3 carbon atom, indicating their *facial* configurations. Similarly ^{19}F NMR spectra gave single resonance, confirming their *facial* structures. A *meridional* structure should give three resonances both for ^{13}C and ^{19}F in the spectra.

When one F atom of $R^2 = CF_3$ is replaced by a H atom the dipole moment of the complexes decreases by about 1.75 D for NiL_2 2.2 D for CoL_3. This large decrease of the moment is due to the big difference in the electronegativities of F and H atoms. The replacement of one F from $R^2 = CF_3$ by a CF_3 group (making $R^2 = C_2F_5$) increases the moments of their square-planar complexes by average 0.38 D, and 0.21 D for CoL_3. This indicates that CF_3 is slightly more electronegative than F atom. By similar line of arguments the electronegativities of the groups can be arranged as $C_3F_7 > C_2F_5 > CF_3 > F$. With same R^2 the dipole moments vary when R^1 arranged as 2′-thienyl > 2′-naphthyl > phenyl.

References

1 M. Das, S. E. Livingstone, S. W. Filipczuk, J. W. Hayes and D. V. Radford, *J. Chem. Soc. Dalton Trans.*, 1409 (1974).

2 M. Das and S. E. Livingstone, *J. Chem. Soc. Dalton Trans.*, 452 (1975).

3 S. W. Filipczuk, J. W. Hayes, D. V. Radford, M. Das and S. E. Livingstone, *J. Chem. Soc. Dalton Trans.*, 886 (1975).

4 M. Das, S. E. Livingstone, J. H. Mayfield, D. S. Moore and N. Saha, *Austral. J. Chem.*, *29*, 767 (1976).

5 M. Das and S. E. Livingstone, *J. Chem. Soc. Dalton Trans.*, 662 (1977).

6 M. Das, *Inorg. Chim. Acta*, *36*, 79 (1979).

7 M. Das, *Transition Metal Chem.*, *5*, 17 (1980).

8 R. Belcher, W. I. Stephen, I. J. Thomson and P. C. Uden, *J. Inorg. Nucl. Chem.*, *34*, 1017 (1972).

9 R. Burton and T. R. Sweet, *Analyt. Chim. Acta*, *64*, 273 (1973).

10 C. S. Saba and T. R. Sweet, *Analyt. Chim. Acta*, *69*, 478 (1974).

11 D. S. Moore, *B. Sc. (Hons) Thesis, University of New South Wales*, 1974.

12 R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-Diketonates and Allied Derivatives', Academic Press, New York (1978).

13 I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

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

15 D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

16 O. Siiman, D. Titus, C. Cowman, J. Fresco and H. B. Gray, *J. Am. Chem. Soc.*, *96*, 2353 (1974).

17 J. Sieler, P. Thomas, E. Uhlemann and E. Hohne, *Z. Anorg. Allg. Chem.*, *380*, 160 (1971).

18 D. C. Craig, M. Das, S. E. Livingstone and N. C. Stephenson, *Cryst. Struct. Comm.*, *3*, 283 (1974).

19 E. A. Shugam, L. H. Shkol'nikova and S. E. Livingstone, *Zhur. Strukt. Khim.*, *8*, 555 (1967).

20 T. Glowiak and T. Ciszewska, *Inorg. Chim. Acta*, *27*, 27 (1978).

21 S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, *12*, 265 (1958).

22 B. F. Hoskins and C. D. Pannan, *Inorg. Nucl. Chem. Lett.*, *11*, 409 (1975).

23 J. Ollis, M. Das, V. J. James, S. E. Livingstone and K. Nimgirawath, *Cryst. Struct. Comm.*, *5*, 679 (1976).

24 R. H. Holm, D. H. Gerlach, J. G. Gordon and M. G. McNamee, *J. Am. Chem. Soc.*, *90*, 4184 (1968).

25 M. Das and D. T. Haworth, *J. Inorg. Nucl. Chem.*, in press.