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Complexes of Dibenzylsulfoxide with the First Series Transition Metal Nitrates*

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Abstract

Under carefully controlled experimental conditions, a series of metal nitrate complexes of dibenzylsulfoxide (DBSO) have been synthesized and isolated (for the dipositive Co, Ni, Cu and Zn elements). The compounds were characterized by use of infrared-, ultraviolet-, and visible spectra. Their stoichiometric compositions appeared to be $[M(DBSO)_3(NO_3)_2]$, where M = Co, Ni and Cu; and $[M(DBSO)_{3.5}(NO_3)_2]$, where M = Zn. The additional information concerning the nature of bonding and structural geometry was derived from X-ray diffraction analysis, molecular conductivities, molecular weight and magnetic susceptibility measurements. The infrared spectra indicated that, in all cases, coordination occurred through the oxygen atom of the DBSO ligand. Both analyses and spectral studies suggest that the transition metal ions manifest a coordination number of six. The slight decrease in metal ion radius across the first transition metal series does not affect the number of DBSO molecules bonded to the M^{2+} ion, but the only variation in total coordination of cation might be attributed to the DBSO competition with nitrato groups for the coordination site due to the ability of the anion to enter the coordination sphere.

Introduction

The ability of sulfoxides as ligands to form stable complexes has been investigated by a number of workers [2]. The syntheses, properties and various physical characteristics of these complexes have been reported.

As a continuation of our work with sulfoxide derivatives [3–5] and in an effort to obtain information regarding the nature of the complexes formed between dibenzylsulfoxide (DBSO) and some first series transition metal nitrates, we recently synthesized a number of new stable transition metal nitrate complexes of DBSO. The complexes have compositions with the general formulas $[M(DBSO)_3(NO_3)_2]$, where M = Co(II), Ni(II), Cu(II) and $[M(DBSO)_{3.5}(NO_3)_2]$, where M = Zn(II). They have been characterized by IR spectra, conductivity and molecular weight measurements, magnetic moments, X-ray diffraction patterns and electronic absorption spectra.

Experimental

Chemicals

The dibenzylsulfoxide ligand was obtained from Aldrich Chemical Company, Inc., in technical grade form, and had to be recrystallized from 50% aqueous ethanol. The melting point for pure crystals is 132–134 °C.

The metal nitrates of the general formula $M(NO_3)_2 \cdot xH_2O$, where $x = 6$ for M = Ni(II), Co(II) and Zn(II); and $x = 2.5$ for M = Cu(II), were obtained from Fisher Scientific Company, Fair Lawn, New York, N.J. They were used as received.

Synthesis

All complexes were prepared by following a slight modification of Weber's method (2(l)) for synthesizing the transition metal perchlorate complexes.

Crystals of the hydrated metal nitrates (≃0.5 mmol) were dissolved in a mixture of four milliliters of t-butanol and a stoichiometric amount of triethylorthoformate, and the compound was stirred with a magnetic stirrer for five minutes at 30–40 °C. Dehydration by this method is described [6] as 98 percent complete with 1:1 mole ratio of water to the hydration reagent, according to the equation:

$$(C_2H_5O)_3CH + H_2O \longrightarrow 2C_2H_5OH + C_2H_5OOCH$$

Triethylorthoformate reacts faster and more completely in polar media than does 2,2-dimethoxypropane. The solution of copper nitrate turned from blue to blue–green at the end of dehydration.

A stoichiometric amount of the ligand DBSO, dissolved in warm t-butanol, was added to the resulting anhydrous solution of the various metal salt solutions, and was well-mixed by stirring. After an

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hour, an equal volume of anhydrous ether was added and the mixture was stirred for thirty minutes at room temperature. The supernatant liquid was then decanted, and the product was stirred in a minimum amount of ether. That was repeated three times. The solid was then filtered, washed with cold anhydrous ether, and dried *in vacuo* over P_2O_5 at room temperature overnight. The yield was 35–45%.

Methods of Characterization

Analytical measurements

Carbon and hydrogen analyses were performed by MicAnal Organic Microanalysis of Tucson, Ariz.

Metal ion analyses were performed by complexometric titration with EDTA, as described by Flaschka [7].

Nitrate analyses were executed by gravimetric precipitation with nitron, as described by Welcher [8].

Total sulfoxide content was determined by following a procedure outlined by Douglas [9]. Standard solutions of potassium permanganate, sodium oxalate and ferrous sulfate were prepared, following the prescribed methods of Kolthoff and Sandell [10], and Day and Underwood [11]. Approximately 30–50 mg of sample were dissolved in 50 ml of 0.5 N sulfuric acid and a few drops of phosphoric acid. An excess of 0.1 N $KMnO_4$ was added to oxidize the sulfoxide to a sulfone. After the reaction, the excess permanganate was reduced to Mn^{2+} by the addition of ferrous sulfate (0.06 N $FeSO_4 \cdot 7H_2O$). The clear solution was then titrated with $KMnO_4$ until a very slight pink color appeared. This is an indirect and accurate method for the total sulfoxide determination.

Physical measurements

Melting points were obtained with a Thomas-Stoover Capillary Melting Point apparatus and were uncorrected.

The IR spectra were obtained from a Perkin-Elmer Model 283B recording spectrophotometer in the region 250–4000 cm^{-1}, while using CsBr plates.

The conductance measurements were made by the use of an Industrial Instrument Model RD 16B2 conductivity bridge, utilizing a conventional conductivity cell containing platinum electrodes. The molecular weight measurements were obtained using a Hewlett-Packard Model 301A vapor pressure osmometer, and were done at 37 °C, with a non-aqueous probe and nitromethane as the solvent. Standard solutions of benzil dissolved in nitromethane were used for a molecular weight calibration curve.

The magnetic susceptibilities were measured by means of a Faraday magnetic balance. Mercury(II) tetrathiocyanate cobaltate(II) provided the magnetic susceptibility standard.

X-ray diffraction patterns were obtained on a General Electric Model XRD-5 and a direct reading diffractometer. A copper K-alpha radiation source was used in conjunction with a nickel filter (λ = 1.54178 Å, at 33 kV, and 15 mA). The sample holder was filled by the method of backpacking [12]. The relative peak heights were the basis for estimating the relative intensities.

The electronic absorption spectra were obtained with two different recording spectrophotometers: a Hewlett-Packard model 8450A (350–800 nm) and a Perkin-Elmer model 559A (190–900 nm). Nitromethane solutions of colored complexes were used to record the visible spectra. Methylene chloride was the solvent for all complexes which absorb light in the ultraviolet region. All measurements were done with 1 cm matched cells. The reflectance spectra of solid compounds were obtained with a Beckman DU spectrophotometer over the wavelength range of 350–1000 nm. The reference standard for obtaining the reflectance spectra was U.S.P. magnesium carbonate.

Results and Discussion

The analytical data and some physical properties of the various metal nitrate complexes are summarized in Table I. The analyses for this series of complexes indicate that no water is present in the composition. From the total analysis, it appeared that these complexes are six-coordinate, which was also confirmed by physical measurements outlined below.

The infrared spectral data for these complexes are summarized in Table II. Early work gave a clear distinction between ionic and coordinated nitrate groups [2(o), 6, 13]. The coordinated nitrate groups give rise to six bands in both infrared and Raman spectra [4]. The nitrate ion exhibits absorption in the infrared at approximately 1390, 830, and 720 cm^{-1}; and in the Raman at 1390, 1050 and 720 cm^{-1}. So it appears that in the transition from an ionic nitrate to a covalent nitrate, a lowering of symmetry occurs, from D_{3h} to C_{2v}, due to the splitting of the four fundamental modes of vibration into six modes, all of which are infrared and Raman active. Strong absorption bands in the regions 1550–1450 and 1290–1250 cm^{-1} in the metal compound containing a nitrate group suggest also that the nitrato group is covalently bound to the central metal atom. Our results, therefore, indicate only coordinated nitrate groups. Unfortunately, however, reports of previous studies give only limited possibilities for distinguishing between symmetrically bidentate nitrato groups and unidentate nitrato groups,

TABLE I. Analytical Data and some Physical Properties of the First Series Transition Metal Nitrate Complexes of Dibenzylsulfoxide

Complex[a]	Theoretical (%)			Experimental (%)			Color	Yield (%)	Melting point (°C)	μ_{eff}(BM) [d]
	M	NO_3	DBSO	M	NO_3	DBSO				
$[Co(DBSO)_3(NO_3)_2]$	6.74	14.19	79.07	6.64	14.03	78.80	pink	34	121	4.78
$[Ni(DBSO)_3(NO_3)_2]$[b]	6.72	14.19	79.09	6.69	14.10	78.70	green	43	123	3.48
$[Cu(BSO)_3(NO_3)_2]$	7.23	14.11	78.65	7.11	13.96	78.50	blue	43	125	2.20
$[Zn(DBSO)_{3.5}(NO_3)_2]$[c]	6.57	12.46	80.98	6.44	12.34	80.66	white	41	124–5	diamag.

[a] DBSO≡$C_{14}H_{14}SO$. [b] Found: C, 58.80; H, 5.19. Calc.: C, 58.30; H, 5.00%. [c] Found: C, 59.67; H, 5.26. Calc.: C, 59.70; H, 5.11%. [d] Measured at 298.2 K, standard deviation ±0.01.

TABLE II. The Infrared Spectral Data[a] for the Dibenzylsulfoxide Complexes of the First Series Transition Metal Nitrates Using CsBr Plates

DBSO	$[Co(DBSO)_3(NO_3)_2]$	$[Ni(DBSO)_3(NO_3)_2]$	$[Cu(DBSO)_3(NO_3)_2]$	$[Zn(DBSO)_{3.5}(NO_3)_2]$	Assignment
	1460(vs)	1460(vs)	1460(vs)	1465(vs)	$\nu_4(NO_3)$
	1320(br)	1320(br)	1320(br)	1320(br)	$\nu_1(NO_3)$
	140	140	140	145	$\Delta(\nu_4-\nu_1)$
1072(m)	1068(m)	1068(m)	1068(m)	1068(m)	$\nu_2(NO_3)$
	1040(w)	1041(w)	1041(sh)	1035(w)	
1030(vs)	1025(vs)	1025(vs)	1026(vs)	1028(vs)	ν_{SO}
	998(sh)	995(w,sh)	1005(sh)	998(m)	
	805(s)	805(s)	805(s)	805(s)	$\nu_6(NO_3)$
	770(s)	770(s)	770(m)	770(m)	$\nu_3(NO_3)$
	718(w)	715(w)	710(w)	718(w)	$\nu_5(NO_3)$
685(s)	695(s)	690(s)	695(s)	695(s)	δ_{CS}
	670(w)	670(w)	670(w)	675(w)	
	588(w)	588(w)	588(w)	588(w)	ring breathing
	505(sh)		510(w)	510(sh)	
468(s)	470(s)	468(s)	470(s)	470(s)	$\delta_{CSO(sym.)}$
	360(m)	360(m)	360(w)	365(w)	$\delta_{CSO(asym.)}$
	320(m)	320(m)	321(m)	325(m)	
			298(w)	298(w)	ν_{MO}

[a] Units cm^{-1}. vs = very strong, s = strong, w = weak, br = broad, m = medium, sh = shoulder.

because the nitrate group is a surprisingly versatile ligand. The assignment of bands, then, has been done with caution, due to the coupling effect between unidentate and symmetrically bidentate nitrato groups. In distinguishing the presence of either or both unidentate and/or bidentate nitrate in these complexes, therefore, attempts were made to correlate $\Delta(\nu_4-\nu_1)$ to the degree of covalency of the nitrate group. Table II also shows that for each complex, there is metal–oxygen bonding because of the $\Delta\nu$(S–O) frequency decrease upon complex formation. The decrease was very small, however, which indicates the probability of a weak bonding, due to an increase in steric crowding. This decrease is also an indication of the drainage of the electron density from the sulfur group towards the coordinated oxygen atom. If $\Delta\nu$(SO) is used as an estimate of the relative metal–oxygen bond strength, in comparison with those determined by Weber [2(l)] for the transition perchlorate complexes of DBSO, it appears that the DBSO ligands are weakly bonded. It is seen from molecular models that DBSO has a large steric requirement. The assignment of ν(M–O) in the DBSO series is difficult because of the large number of aromatic vibrations below 600 cm^{-1} (Fig. 1). Weber [2(l)] tried to give the relationships in an attempt to assign ν(M–O) in DBSO. He concluded that as the mass of the ligand increases, ν(M–O) decreases. Thus, ν(MO) should be lower than the 325 cm^{-1} frequency found in analogous pyridine N-oxide complexes [14]; also as the coordination number of the complexes with the same ligand decrease, ν(M–O) increases. This was not easily distinguishable in our studies here. The assigned CSO bonding fundamentals at 481 and 303 cm^{-1} are based on Green's study of DPSO complexes [15].

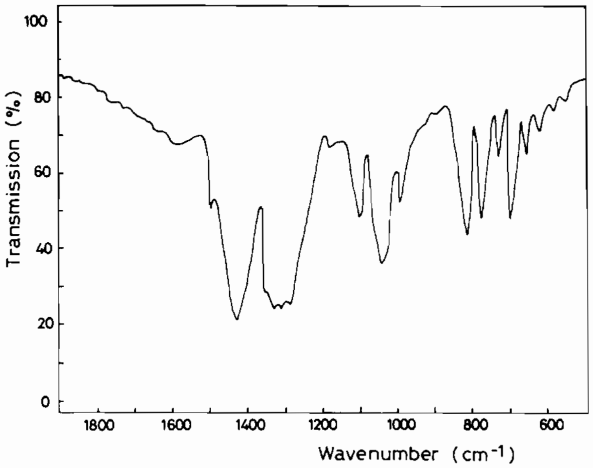

Fig. 1. The infrared spectrum for the transition metal nitrate complexes (a typical example of co-complexes).

By comparison, the 470 and 320 cm^{-1} bands in our DBSO complexes are in good agreement. These bands increased upon complexation.

The assignment of the C–S stretching vibration in sulfoxide with an aryl-substituted group is more difficult. According to Bellamy [13d], the C–S stretching vibration of the arylsulfoxides occurs in the 702–607 cm^{-1} region. He assigned a very weak band near 670 cm^{-1} for C–S stretching vibration in DPSO and phenylmethylsulfoxide. In his complexes, the assignment was even more difficult because of the very intense bands of the C–H out-of-plane deformation modes of vibration, which occurred near 750 and 700 cm^{-1}. In good agreement, our complexes in this study have a C–S stretching vibration near 670–695 cm^{-1} for the transition metal nitrate complexes. Srivastava and coworkers [2(o)] found that the C–S stretching absorption undergoes a slight positive shift on complexation from 685 to 700 cm^{-1}, which is an indication in our complexes of the decrease in the double bond order of the SO group and an electron shift from the aryl group to the sulfur atom of the ligand.

Geary [16] has compiled acceptable ranges for complexes of approximately 10^{-3} M concentration in nitromethane for various types of electrolytes: 1:1 is 75–95; 2:1 is 150–180; 3:1 is 200–260; and 4:1 is 290–330 ohm^{-1} cm^2 mol^{-1}. The specific conductance data for the DBSO complexes of the transition metal nitrate in nitromethane solvent, reported in Table III, lie within the range 3.7–7.0 ohm^{-1} cm^2 mol^{-1}. The data suggests that these complexes are non-electrolytes and neutral species, and that the nitrato groups are strongly bound to the metal ion. Their molecular weight measurements are also summarized in Table III. The results show the presence of one particle in CH_3NO_2 (with reference to the empirical formula). At the moment, there is a feeling that the Zn(II) complex may have a non-monomeric character, as evidenced by its fractional formula and lack of conductivity, which satisfy both the stoichiometric and stereochemical requirements. Reconciling such non-monomeric character with the molecular weight data may prove difficult. It should be noted that nitromethane was recommended as a solvent because it has weak donor properties, and consequently, all electrolytes exhibit relatively high conductivities in it. So far, it is conclusive that there is no ionic nitrate group.

Magnetic moments for the solid compounds at room temperature, corrected for diamagnetic contributions, are presented in Table I. The magnetic moments of the cations of the first d-type transition series are determined largely by the number of unpaired d-electrons. Since these electrons also participate in bond formation, orbital contributions are diminished by the bonded groups, and the observed magnetic moments are a function of electron spin only [17]. The magnetic moments for the six-coordinate complexes of Ni(II) and Cu(II) complexes fall within the ranges previously reported for octahedral high-spin complexes [18], with the exception

TABLE III. Conductance and Molecular Weight Data for the First Series Transition Metal Nitrate Complexes of Dibenzylsulfoxide in Nitromethane

Complex	Concentration (mM)	Λ_m (ohm^{-1} cm^2 mol^{-1})^a	Apparent molecular weight^b	Actual formula weight
$[Co(DBSO)_3(NO_3)_2]$	4.02	3.66	868.54	873.92
	2.02	5.11	859.00	
$[Ni(DBSO)_3(NO_3)_2]$	4.00	4.23	870.00	873.70
	2.02	5.54	858.13	
$[Cu(DBSO)_3(NO_3)_2]$	3.98	4.31	871.92	878.54
	2.00	6.00	870.90	
$[Zn(DBSO)_{3.5}(NO_3)_2]$	4.02	4.23	984.50	995.55
	2.02	6.18	981.49	

^{a}Measured at 25 °C. ^{b}Measured at 37 °C.

of $[Co(DBSO)_3(NO_3)_2]$. The range of accepted magnetic moments for octahedral high-spin Co(II) complexes has been reported to be 4.8–5.2 BM. Its reduction in our results, to 4.78 BM, suggests the removal of orbital degeneracy, which arises from some form of strong coupling between the unpaired electrons on adjacent metal atoms through exchange forces. Our result for the Co(II) nitrate compound is in good agreement with the one obtained by Navarro-Ranniger *et al.* [19] for the octahedral $[Co(MPMB)_2(ClO_4)_2$ compound. Other reported octahedral Co(II) nitrate compounds, $[Co(C_5H_5NO)_6](NO_3)_2$ [20a] (μ_{eff} = 4.77 BM); $[Co(C_5H_5NO)_2(NO_3)_2]$ [20b]; and $[Co(Me_3PO)(NO_3)_2]$ [20c], have similar geometrical structure. This reduction behavior was attributed to spin–orbit coupling and concomitant geometrical distortion [20]. Additional information concerning the cause of magnetic moment reduction is discussed by Burstall and Nyholm in their early report [21], which bases their conclusion on an ionic and covalent octahedral bonding concept.

The powder X-ray diffraction data can be found in Table IV. The interplanar spacings were calculated using the Bragg equation, and the relative intensities were derived from the intensities of the major peak in the spectrum. The X-ray data suggest that these complexes are isomorphous because of the similarity

TABLE IV. X-ray Data for the Dibenzylsulfoxide Complexes of the First Series Transition Metal Nitrates

Co		Ni		Cu		Zn	
d (Å)	I/I_{100}	*d* (Å)	I/I_{100}	*d* (Å)	I/I_{100}	*d* (Å)	I/I_{100}
13.04	13.0	12.96	19.0			13.04	60.0
				9.76	72.0		
				7.49	58.0		
				7.09	25.0		
6.57	4.0	6.57	4.0	6.47	8.0	6.58	13.0
				5.90	4.0		
				5.28	6.0		
				4.93	27.0		
4.40	100.0	4.38	100.0	4.40	38.0	4.40	100.0
4.21	8.0	4.21	10.0	4.26	11.5	4.22	5.5
				4.14	30.0		
3.95	10.0	3.95	5.5	3.95	10.0	3.96	6.0
				3.85	5.0		
				3.68	26.0		
3.40	24.5	3.39	18.0			3.39	17.0
3.34	10.0	3.34	7.0	3.23	19.0	3.31	8.5
				3.04	8.0		
				2.97	4.0		
2.88	5.5	2.88	4.5	2.89	4.0	2.88	3.5
				2.80	4.5		
2.65	8.5	2.65	26.0			2.65	28.9

TABLE V. Visible Spectral Data for the Colored Dibenzylsulfoxide Complexes of the First Series Transition Metal Nitrates and Derived Electronic Parameter for Nickel(II) Complex

Complex	Assignment	Using CH_3NO_2 medium		Using solid reflectance	
		λ (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ (nm)	ϵ_{max} (M^{-1} cm^{-1})
Co	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	540	28.21	483	
	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$			532	
Ni[a]	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	406	38.00	402	
	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	655	23.10	648	
Cu	$^2E_g \rightarrow {}^2T_{2g}$	400	30.72	750	
		730	21.11		

[a] $\nu_3[^3A_{2g}(F) \rightarrow T_{1g}(P)]$, 24 630 cm^{-1}; $\nu_2[^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)]$, 15 267 cm^{-1} and $\nu_1[^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)]$, 9600 cm^{-1} (obs.); 9570 cm^{-1} (calc.); Dq = 957.4 cm^{-1}; B = 745 cm^{-1}; and β = 0.89.

of their d-spacings and intensities. This is another confirmation that these transition metal complexes are isostructural and six-coordinated in geometry.

The electronic absorption spectral data for the dibenzylsulfoxide complexes of the transition metal nitrates are given in Table V. These spectral data were found to be almost the same in the solid as in solution, and the bands are broad. The molar absorptivities are within the acceptable range for octahedral complexes. For octahedral Co(II) complexes, three bands are expected, especially in the reflectance spectra corresponding to the three spin-allowed transitions: ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$; ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$. All these transitions are dominated by the highest-energy transition, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, that ususally overlaps with the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition, because they are very close in energy and therefore the latter is not observed [22]. Its observation in the solid reflectance spectra might be an indication that the octahedral DBSO complexes experience considerably more distortion in the solid than in solution [23]. Another reason for not observing it may be the fact that it is a two-electron transition, and therefore of low intensity [19, 24]. The third transition, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, is expected to occur in the near-infrared and is normally weaker than the other two transitions [25]. The spectral assignments are not straightforward, due to poor resolution and occasional low intensity, in other examples.

In the case of the octahedral nickel(II) complex, three spin-allowed transitions are also expected. However, only two transitions, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, can be observed in the visible range. The third electronic transition, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, can only be expected in the near-infrared region. The spin-forbidden transition is assigned as ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$. The information regarding the ligands electrostatic interaction and the degree of covalency with the Ni(II) ion is tabulated in Table V. Our octahedral Ni(II) complex spectra are in good agreement with those obtained by Askalani and Genena for some oxygen-ligated octahedral Ni(II) species [26].

The ground state of an octahedral coordinated Cu(II) ion is doubly degenerate $[{}^2E_g(t_{2g})^6(e_g)^3]$, and the excited state is triply degenerate, $[{}^2T_{2g}(t_{2g})^5(e_g)^4]$. This indicates that the electronic transition is ${}^2E_g \rightarrow {}^2T_{2g}$, which causes the motion of a positive hole from e_g level to the t_{2g} level [27]. As a whole, the number of bands and their positions show octahedral coordination in all complexes studied.

Conclusions

Both analyses and spectral studies suggest that the transition metal ions manifest a coordination of six, and the nitrate groups are coordinated. The variability in coordination number of ligands indicates competition between the nitrate ion and DBSO groups for the coordination site. The compact packing of the crystals can also contribute to a lowering of the number of bulky DBSO groups coordinated. It is also significant that the nitrate group has sufficient donor strength for the DBSO groups to 'make room' for it in the coordination sphere. The reduction of magnetic moment in Co(II) complexes is attributed to: the splitting of the ground state, due to an axial field component; the spin–orbit coupling constant; and also the parameter which allows for the reduction of orbital angular momentum, due to electron delocalization. Complexes are all octahedral in shape.

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