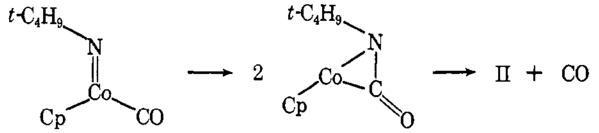
any known polynuclear cobalt complexes.[1,12,13] The two nitrogen atoms of II are quadruply σ bonded as in I whose internickel distances (2.21–2.34 Å) are the shortest so far that we are aware of. The significantly different metal–nitrogen distances in compounds I and II appear to be due to a change in the organic moiety attached to the nitrogen atom.

Complex II may be regarded as an intermediate of the formation of N,N′-di-*t*-butylurea found in the sulfurdiimide reaction. A reasonable explanation for the formation of II may be found if one assumes an insertion reaction of a carbonyl ligand into the cobalt–nitrene bonding producing an unstable isocyanate complex.



A reaction bearing on this mechanism appears to be the interaction of phenylisocyanate with triiron dodecacarbonyl which was reported to give a presumably isostructural complex, $[(C_6H_5N)_2CO]Fe_2(CO)_6$.[14]

Acknowledgment.—The authors are indebted to Takeda Chemical Industries Ltd. for making a Hilger and Watts linear diffractometer and the mass spectrometer available. We are grateful to Professor T. Watanabe of Kansei Gakuin University for the valuable suggestion on the analysis of X-ray diffraction data.

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Transition Metal N,N-Diethyldiselenocarbamates

BY C. FURLANI, E. CERVONE, AND F. DIOMEDI CAMASSEI

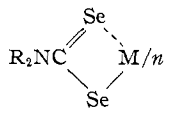
Received August 2, 1967

Transition metal complexes of dsc (N,N-diethyldiselenocarbamate) have been prepared with Cr(III), Co(III), Ni(II), and Pd(II), and their electronic spectra, together with those of the already known Cu(II) and Zn(II) complexes, have been investigated and interpreted in terms of a ligand field model. The spectrochemical and nephelauxetic position and the optical electronegativity value of the dsc ligand are discussed and compared with those of the analogous sulfur-containing ligand dtc.

Introduction

Among the heavy donor atoms, selenium is one of the least widely investigated. There has been some recent interest in Se-containing complexes, *e.g.*, of diselenophosphates,[1] of diselenetene and diselenato complexes,[2] of alkyl or aryl selenides,[3–5] of selenides in ZnSe or CdSe lattices,[6,7] and of selenoureas,[8–10] but as a whole our knowledge of selenium as donor atom in metal complexes is far less detailed than that of the homologous element sulfur. As a part of a research program on complexes with soft donor atoms we have studied the interesting ligand, N,N-diethyldiselenocarbamate ($(C_2H_5)_2NCSe_2^-$ = dsc), first prepared by Barnard and Woodbridge.[11] In particular we have prepared some new transition metal complexes besides the zinc and copper compounds already described by Barnard and Woodbridge[11] and have investigated particularly their spectrochemical properties.

The chemistry of complex diethyldiselenocarbamates is, as we can judge from our results, completely analogous to that of the dialkyldithiocarbamate complexes. Thus the free ligand (sodium or potassium salts, prepared from carbon diselenide and diethylamine in basic medium) reacts readily with several transition metal salts or complexes, giving monomeric, nonelectrolytic inner complexes, which are generally of the low-spin type and highly colored, much like the corresponding dialkyldithiocarbamato complexes, and contain four-membered chelate rings



We prepared and investigated the diethyldiselenocarbamates of Cr(III), Co(III), Ni(II), and Pd(II), in addition to the already known Cu(II) and Zn(II) complexes. All of these complexes are remarkably stable for selenium-containing compounds; only the Cr(III) compound undergoes decomposition more easily. The electronic spectra of such complexes resemble closely those of the corresponding dithiocarbamates, except for a general red shift of all transitions. The similarity between the chemical behavior of the

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(5) S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

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(7) R. S. Title, *ibid.*, **130**, 17 (1963).

(8) A. T. Pilipenko and I. R. Sereda, *Zh. Analit. Khim.*, **13**, 3 (1958).

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TABLE I

SUMMARY OF DATA ON METAL N,N-DIETHYLDISELENOCARBAMATES

		Analyses, %													
		C		H		N		Metal			Mol wt[a]				
Compound	Color and crystal habit	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	μ, BM	Found	Calcd	Solubility[b]	Mp, °C	Previous reports
K(dsc)	Yellow-orange needles	21.30	21.30	3.50	3.55	4.98	4.96	...	13.95	...	...	281	s diox vs chl, ac	134	
$Zn(dsc)_2$	Pale yellow monoclinic prisms	See ref 10								Diam	521	550	s xyl, ac vs chl	154–155	Ref 11
$Ni(dsc)_2$	Deep green-brown monoclinic prisms	21.95	22.10	3.36	3.68	5.08	5.16	10.96	10.82	Diam	544	543	s bz, xyl, dmf vs chl	255–256	
$Pd(dsc)_2$	Red-orange prisms	20.19	20.34	3.50	3.41	4.91	4.74	...	18.02	Diam	583	591	s chl, ac	275–277	
$Cu(dsc)_2$	Red-brown monoclinic prisms	22.30	21.95	4.00	3.68	...	5.12	...	11.60	1.79	498	548	s ac vs chl	225–226	Ref 11
$Cr(dsc)_3$	Blue-gray prisms	23.21	23.15	4.00	3.89	5.48	5.40	6.58	6.68	3.87	707	778	s ac vs chl	275 dec	
$Co(dsc)_3$	Deep red-brown prisms	22.96	22.95	3.96	3.83	5.39	5.35	7.15	7.51	Diam	744	785	s ac, am-OH vs chl	285 dec	

[a] Osmometric in chloroform solution. [b] s = soluble; vs = very soluble; ac = acetone; chl = chloroform; diox = dioxane; bz = benzene; xyl = xylene; dmf = dimethylformamide; am-OH = amyl alcohol.

complex thio- and selenocarbamates is remarkable (*e.g.*, $Ni(dsc)_2$ does not give appreciable formation of a paramagnetic 1:2 adduct with pyridine, like $Ni(dtc)_2$, but unlike all other square-planar Ni(II) complexes with four sulfur ligands), and there is a corresponding similarity in structure. X-Ray investigations by Bonamico and coworkers[12] have shown that $Ni^{II}(dsc)_2$ is isomorphous and isostructural with $Ni^{II}(dtc)_2$; $Cu(dsc)_2$ is isomorphous with $Cu(dtc)_2$, as is $Zn(dsc)_2$ with $Zn(dtc)_2$. A possible difference, apart from the spectroscopic ones which we shall discuss below, occurs for the Fe(III) compounds, since $FeCl(dsc)_2$ ($S = {}^3/_2$) appears much more stable and easily formed than $Fe(dsc)_3$, whereas for the dithiocarbamates, the two types of compounds are of comparable stability.[13] We shall report in a subsequent note the composition and properties of iron(III) diethyldiselenocarbamates.

Experimental Section

Preparation of Ligand.—The preparative method of the ligand differs slightly from the procedure of Barnard and Woodbridge.[11]

The required amount of carbon diselenide has been prepared and purified according to Gattow and Dräger.[14]

Into a 250-ml round-bottomed flask, bath cooled at about $-10°$ and fitted with a stirrer, was poured a sodium hydroxide solution (1.2 g in 40 ml of H_2O), and then a flow of nitrogen was admitted for about 0.5 hr. Then a slight excess of amine was added, and finally, very slowly (about 2 hr) and stirring vigorously, a solution of carbon diselenide in dioxane (4.2 g in 40 ml) was added. In order to avoid possible insoluble impurities coming in general from polymerization of carbon diselenide, the solution was filtered and used for the preparation of complexes.

From the same solution were separated by extraction with chloroform sodium and potassium salts, which were mentioned as intermediates but were not isolated by Barnard and Woodbridge.[11]

Preparation of Complexes.—The resulting solution of Na(dsc) or K(dsc) was mixed with an aqueous solution of the appropriate metal chloride or chloro complex in stoichiometric amounts (cobalt can be added in bivalent form but owing to fast autoxidation the complex of the tervalent element is invariably obtained). Upon such treatment some complexes ($Zn(dsc)_2$, $Co(dsc)_3$) precipitated spontaneously, while some others ($Cu(dsc)_2$, $Ni(dsc)_2$, $Cr(dsc)_3$, $Pd(dsc)_2$) had to be extracted from the water–dioxane mixture with chloroform. In every case the raw products could be easily crystallized from several solvents, *e.g.*, acetone or dimethylformamide.

Results and Discussion

The dsc complexes prepared by us are generally deeply colored substances, whose analytical and other relevant properties are listed in Table I; they are remarkably stable, can be kept indefinitely either in air or under vacuum when they are in pure crystalline state, and are not particularly sensitive to oxygen or humidity when in solution. They are readily soluble (as monomeric nonelectrolytes, except of course the saltlike sodium and potassium compounds) in polar organic solvents, particularly chloroform, benzene, and acetone; they are either not very soluble or insoluble in water; the solutions have negligible electric conductivity.

Electronic Spectra.—The absorption spectrum of solutions of K(dsc) consists of two intensive ultraviolet bands at 34.4 kK (log ϵ_{mol} 4.48) and 32.2 kK (log ϵ_{mol} 4.25), with a shoulder at 27.0 kK (log ϵ_{mol} 3.32) and possibly some very weak forbidden transitions at 22.5 kK (log ϵ_{mol} 2.60). It is to be noticed that such a spectrum is rather similar to that of the dialkyldithiocarbamate ions (*e.g.*, $Zn(dtc)_2$[15] has two intense ultraviolet bands at 38.4 kK (log ϵ_{mol} 4.53) and at 35.5 kK (log ϵ_{mol} 4.20)), but shifted some 3–4 kK to the red, so that the most intense absorption lies in the visible (violet) portion of the spectrum. The free ligands thus appear yellow or orange.

The absorption pattern of the ligand is repeated rather regularly in all transition metal compounds of dsc^- (see Table II and Figures 1 and 2), thus facilitating identification of the ligand field spectrum and in some instances also of charge-transfer transitions. Somewhat larger deviations in the patterns of ligand absorption bands are exhibited by the species $Ni(dsc)_2$ and $Pd(dsc)_2$, possibly as a consequence of stronger interligand conjugation in planar moieties (this probably does not apply to $Cu(dsc)_2$, since copper(II) compounds of this type often tend to distorted geometries; *e.g.*, $Cu(dtc)_2$[16]).

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[12] M. Bonamico and G. Dessy, *Chem. Commun.*, 21, 1114 (1967).

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[14] G. Gattow and M. Dräger, *Z. Anorg. Allgem. Chem.*, **343**, 12 (1966).

[15] H. P. Koch, *J. Chem. Soc.*, 401 (1949).

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TABLE II

SPECTRAL DATA OF METAL N,N-DIETHYLDISELENOCARBAMATES[a]

Compound	d–d	Charge transfers	Ligand bands I	Ligand bands II	Notes
$K(dsc)$	. . .	. . .	32.2 (4.25)	34.4 (4.48)	sh at 22.5 (2.60) and at 27.0 (3.32)
$Zn(dsc)_2$	. . .	. . .	31.5 (4.11)	35.0 (4.41)	sh at 27.9 (3.18)
$Ni(dsc)_2$	14.8 (2.06); 18.4 (2.17)	[21.1] (3.30); 23.3 (3.91)	27.9 (4.52)	38.8 (4.65)	sh at 31.5 (3.81) and at 36.4 (4.30)
$Pd(dsc)_2$	20.6 (2.48)	25.8 (2.82)	30.7 (4.85)	37.9 (4.11)	sh at 34.3 (4.19)
$Cu(dsc)_2$	[16.7] (3.41)	20.2 (4.06)	30.9 (4.20)	34.5 (4.50)	. . .
$Cr(dsc)_3$	14.8 (2.72); 19.1 (2.65)	[25.5] (3.82); 28.0 (4.25)	[30.8] (4.31)	33.6 (4.65)	sh at 12.7 (1.96) and at 18.0 (2.52)
$Co(dsc)_3$	14.4 (2.81); [19.1] (3.10)	[22.2] (4.23); 24.6 (4.41)	28.7 (4.63)	32.3 (4.82)	. . .

[a] Solvent: chloroform. Band maxima are in kK (log ϵ_{mol}); shoulders are in brackets.

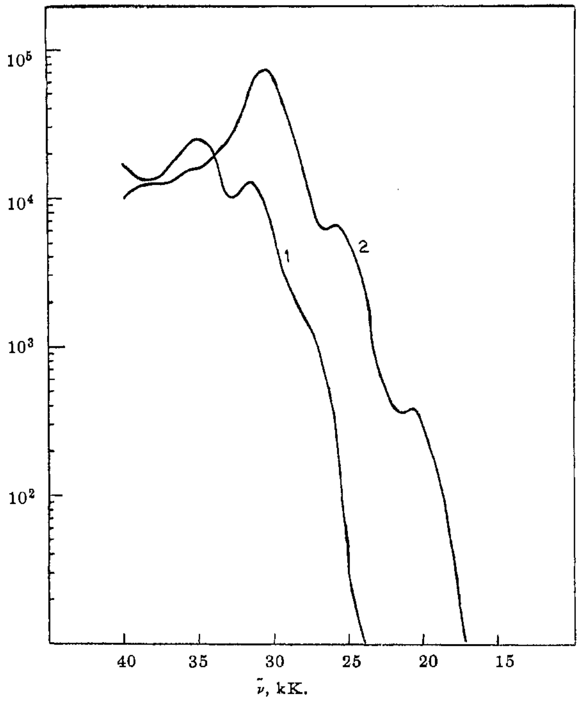

Figure 1.—Absorption spectra of $Zn(dsc)_2$ (1) and $Pd(dsc)_2$ (2); solvent, chloroform.

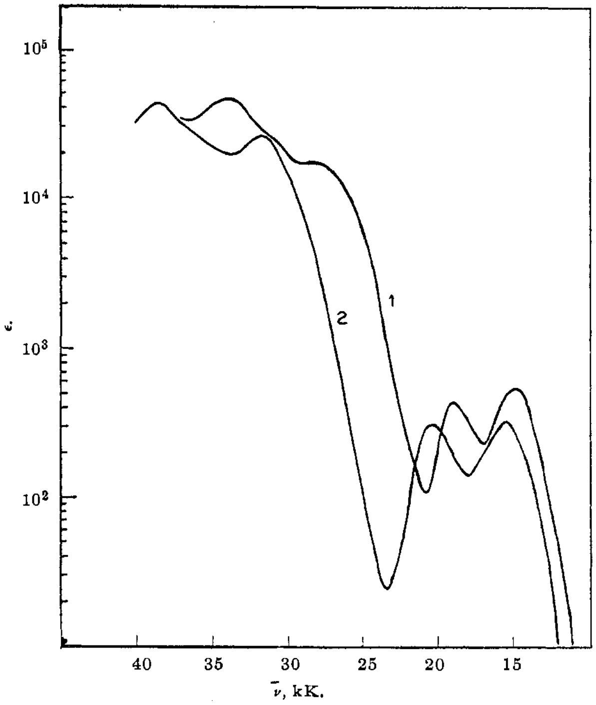

Figure 2.—Comparison of the absorption spectra of a thio and a seleno complex: $Cr(dsc)_3$ (1) and $Cr(dtc)_3$ (2) in chloroform solution (dtc = N,N-diethyldithiocarbamate).

We now discuss separately the spectrochemical, nephelauxetic, and optical electronegativity values emerging from the data of Table II. The position of the dsc^- ligand in the spectrochemical series of octahedral complexes can be inferred from $\Delta = 14.8$ kK for $Cr(dsc)_3$ and 14.4 kK for $Co(dsc)_3$, as compared with $\Delta = 15.5$ kK for $Cr(dtc)_3$ and 15.5 kK for $Co(dtc)_3$. Diselenocarbamates have therefore only slightly lower ligand field strengths than the corresponding dithiocarbamates, but in other thio ligands (*e.g.*, $\Delta = 14.3$ kK for $Cr(dtp)_3$ (dtp = diethyldithiophosphate)) still smaller ligand field strengths occur. The same trend is revealed by the spectra of the square complexes: $\bar{\nu}_1$ for $Ni(dsc)_2$ at 14.8 kK is lower than for $Ni(dtc)_2$ (15.8 kK) but higher than for $Ni(dtp)_2$ (14.5 kK). A similar trend occurs with $Pd(dsc)_2$ ($\bar{\nu}_1$ at 20.6 kK) compared with 22.2 kK of $Pd(dtc)_2$; here, however, the value for $Pd(dtp)_2$ is higher (21.8 kK). Spectrochemical differences between S and Se donors of comparable sign and magnitude have been reported for dialkyldithio- and diselenophosphates,[1] and between thio- and selenoureas.[10] The position of dsc^- in the more extensive spectrochemical series of octahedral chromophores would be

$$Br^- < dsp^- \lesssim Cl^- < dtp^- < dsc^- < F^- \lesssim \text{urea} < dtc^- < xant^- < H_2O < NH_3$$

It is in our opinion rather unexpected that the spectrochemical difference between S and Se is so small, in consideration of both the much sharper differences P > As and Cl > Br in the neighboring groups and of the presumably smaller σ-antibonding effects on the d-shell orbitals in selenium- than in sulfur-containing complexes (the overlap of Se with metal orbitals is smaller than that of S; *e.g.*, the overlap $3d\sigma$–$np\sigma$, calculated for the neutral atoms using the orbital functions by Richardson,[17] by Clementi,[18] and by Watson and Freeman,[19] turns out to be 0.104 between Co and S (n =

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[18] E. Clementi, *ibid.*, **41**, 303 (1964).

[19] R. E. Watson and A. J. Freeman, *Phys. Rev.*, **123**, 521 (1961).

3) at 2.2-Å internuclear distance, but only 0.095 between Co and Se ($n = 4$) after allowing for the larger atomic radius of Se). A possible explanation could be reached on the assumption that π back-donation, lowering the energy of $d\pi$ orbitals, occurs to a larger extent with Se than with S ligands.

The nephelauxetic effect estimated from the energy difference between the first two d–d bands of $Cr(dsc)_3$ and the first two of $Co(dsc)_3$ yields $\beta_{35} = 0.41$ in the former and 0.36 in the latter case. These are remarkably low values, in agreement with previous reports that selenium donors are able to cause a much more pronounced nephelauxetic decrease than the corresponding sulfur-containing ligands.[1]

Determination of the optical electronegativity of dsc^- is uncertain because of the difficulty of assigning exactly the charge-transfer bands in the presence of intense ligand bands. Probably the best guess can be made from the spectrum of $Co(dsc)_3$, which has a charge-transfer band at 22.2 kK, corresponding, after the correction $(-\Delta + D)$, to a σ_{cor} value of 9.9 kK; *i.e.* $\chi_{opt}(dsc^-) \sim 2.68$ if we assume $\chi_{opt}(Co) = 2.35$.[20]

Identification of the true charge transfer $\pi \rightarrow e_g$ is very uncertain in the complex spectrum of the Cr(III) compound. The charge transfer at 26.1 kK in $Pd(dsc)_2$, if compared with the first charge transfer of $[PdBr_4]^{2-}$ at 30.2 kK and of $[PdI_4]^{2-}$ at 20.5 kK, leads to χ_{opt} (dsc) $\sim$ 2.6. Thus all data point, although somewhat unclearly, to an χ_{opt} of Se in dsc^- between 2.6 and 2.7, almost imperceptibly lower than that of S in dtc^- (2.7 according to ref 21). In a parallel comparison, $\chi_{opt} = 2.7$ for $(C_2H_5O)_2PS_2^-$ and 2.6 for $(C_2H_5O)_2PSe_2^-$, the difference in χ_{opt} between S and Se is already small (0.1). Here it is even smaller, and in our opinion they might be a consequence of extensive π bonding between metal and ligand, including also π back-donation and resulting in a lowering of the filled π orbitals of the ligands.

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Metal Complexes as Chelates. II. Binuclear Complexes Containing Similar and Dissimilar Metal Atoms[1]

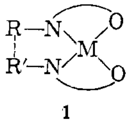
BY S. J. GRUBER, C. M. HARRIS, AND E. SINN

Received July 24, 1967

A new series of oxygen-bridged complexes is reported with special emphasis on copper(II). Most of these complexes can be shown to be discrete dimeric molecules. Both homo- and heteronuclear dimers can be prepared in a large number of cases, by forming a complex of metal M with a tetradentate salicylaldimine, L, and, in turn, using this complex itself as a ligand. The latter (ML) then acts as a bidentate in complexing with a metal halide, MX_2 or $M'X_2$, to which it coordinates through its two phenolic oxygens. The Schiff base complexes used here as ligands ("complex ligands") are tetradentate Schiff base complexes of copper(II) and nickel(II). The former are normal paramagnetics, in contradistinction to reports of anomalous magnetic moments, and the latter are well known to be diamagnetic. The binuclear complexes are generally considerably less soluble in organic solvents than the complex ligands, so that many different complexes can be formed by direct reaction in saturated solutions. Both the complex ligands and the binuclear complexes are nonionic in nitrobenzene. All of the homonuclear complexes of copper(II) show antiferromagnetic interactions, which can readily be explained in terms of the well-established "Bleany–Bowers" theory. Heteronuclear complexes so far prepared involving copper(II) with other paramagnetic and diamagnetic metals and nickel(II) with other paramagnetic metals are simple paramagnetics and their magnetic properties are in accord with the Curie–Weiss law, between 80 and 400°K, with relatively small Weiss constants.

Introduction

Solutions of various metal salicylaldimines (1) and metal halides reacted in organic solvents to form new types of complexes to which we attribute an oxygen-bridged structure (2). In this way it is possible to bring almost any two metals, similar and dissimilar, into combination.[1,2] Various types of trinuclear complexes involving both similar and dissimilar metals, were prepared using an analogous method, but with noncoordinating anions such as perchlorate replacing the halogen atoms.[1,2] Oxygen bridging of the type shown in structure 2 brings groups of two or three metal atoms into close proximity so that antiferromagnetic interactions occur in a number of cases where the metals have unpaired electrons. The shifts observed in the infrared frequencies associated



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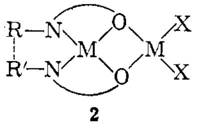

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(1) (a) Part I: S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nucl. Chem. Letters*, **3**, 496 (1967); (b) taken in part from the Ph.D. thesis of S. J. Gruber, University of New South Wales, 1966. Preliminary work was reported in the B.Sc. (Honors) thesis of S. J. Gruber, 1962.

(2) S. J. Gruber, C. M. Harris, and E. Sinn, to be published.