two stereoisomers. This conclusion should also apply to complexes with identical ligand structures. The observed variations of $\Delta\Delta H$ with ligand structure imply that $\Delta\Delta H_{\mathrm{Co-Ni}}{}^{\mathrm{t-p}}$(CFSE) is not the sole contributing factor to the stability differences. Values of stability differences corrected for CFSE effects could not be obtained.

Finally, the complexes $\mathrm{Fe(R{-}C_6H_5HCH_3)_2}$ (R = H, $\mathrm{CH_3}$) have been prepared and found to be tetrahedral in chloroform solution.[5] Provided that the planar configuration of these complexes possesses an energy minimum, this result, together with those reported herein, demonstrates that the relative stability of the planar form increases in the sequence Ni(II) > Co(II) > Fe(II). Further results concerning the four-coordinate stereochemistry of divalent ions other than Ni(II) and Co(II) will be reported in a future publication.

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CONTRIBUTION FROM THE MCPHERSON AND EVANS CHEMICAL LABORATORIES,
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Reactions of Coordinated Ligands. XVIII. Metal Ion Control in the Synthesis of Octahedral Nickel(II) Complexes of α-Diketobis(3-aminopropylimines)

BY LARRY T. TAYLOR,[1] NORMAN J. ROSE,[1] AND DARYLE H. BUSCH

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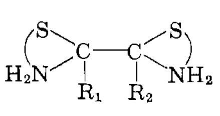
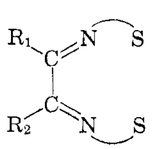
The reaction of α-diketones with 1,3-diaminopropane in the presence of nickel(II) salts yields a new family of chelate compounds. The new ligands 2,3-butanedionebis(3-aminopropylimine) (BTM), 2,3-pentanedionebis(3-aminopropylimine) (PTM), and 1,2-cyclohexanedionebis(3-aminopropylimine) (CTM) could not be prepared in the absence of the metal ion. The metal ion is six-coordinate in the thiocyanate and $\mathrm{ZnCl_4{}^{2-}}$ derivatives, $\mathrm{NiL(NCS)_2}$ and $\mathrm{NiL(ZnCl_4)}$, and in solution in a variety of solvents. The ligands exert a strong ligand field, having an average Dq^{xy} = 1228 cm^{-1}. Infrared spectra reveal that the thiocyanate anions are N bonded and occupy *trans* positions in the coordination sphere of the metal ion. Both symmetric and asymmetric stretching modes are observed for the $-\mathrm{N}{=}\overset{|}{\mathrm{C}}\overset{|}{\mathrm{C}}{=}\mathrm{N}-$ grouping.

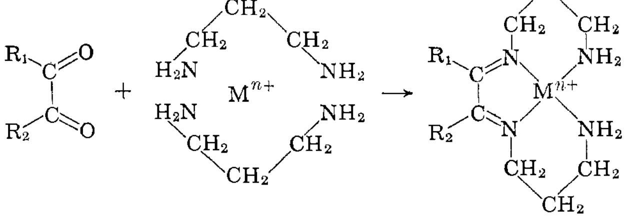
Introduction

In recent years there has been an increased interest in the area of ligand reactions[2] This has been accompanied by a growing awareness of the fact that metal ions often permit the facile synthesis of coordinated ligands in cases where the free organic materials either are not accessible by separate synthesis or can be prepared only by lengthy and wasteful routes These developments have led to the characterization of several new categories of chelate derivatives. Examples of this type of process include: (1) the reaction of polyamines with ketones,[3] aldehydes,[3] hydroxy ketones,[4] α,β-unsaturated ketones,[4] and 2,6-diacetylpyridine;[5] (2) the reaction of coordinated mercaptides with dibromoalkanes;[6] and (3) the reaction of mercaptoamines with α-diketones.[7] Depending on the example, the latter reaction may proceed best by either the initial formation of a thiazolidine (I), which rearranges in the presence of a metal ion to give the corresponding Schiff base chelate (II),[8] or by condensation of the mercaptoamine and α-diketone in the presence of the metal ion.[7]


I


II

One of the more obvious routes to chelate ring formation is the reaction of a diamine with an α-diketone in the presence of a metal ion. Although a variety of early attempts to utilize this reaction failed to yield characterizable compounds,[9] we have succeeded in the synthesis of new chelate compounds by this method.



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[1] National Institutes of Health Postdoctoral Fellows, 2-F2-GM-28,091-02 and 4-F2-GM-28,191-02.

[2] D. H. Busch, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 1; M. M. Jones and W. A. Connor, *Ind. Eng. Chem.*, **55**, 15 (1963); Q. Fernando, *Advan. Inorg. Chem. Radiochem.*, **7**, 185 (1965); J. P. Collman, *Transition Metal Chem.*, **2**, 2 (1966).

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[6] M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

[7] M. C. Thompson and D. H. Busch, *ibid.*, **86**, 213 (1964).

[8] H. Jadamus, Q. Fernando, and H. Freiser, *ibid.*, **86**, 3056 (1964).

[9] D. H. Busch, Thesis, University of Illinois, 1954.

Experimental Section

Materials.—1,3-Diaminopropane, 2,3-butanedione, and 1,2-cyclohexanedione were obtained from Aldrich Chemical Co., Inc., and 2,3-pentanedione was obtained from Matheson Coleman and Bell. All other chemicals and solvents were of reagent grade or equivalent.

Preparation of 2,3-Butanedionebis(3-aminopropylimino)-nickel(II) Tetrachlorozincate.—1,3-Diaminopropane (4.44 g, 0.06 mole) was added to a solution prepared by adding $NiCl_2 \cdot 6H_2O$ (7.13 g, 0.03 mole) to 400 ml of anhydrous methanol. To this solution was added 2,3-butanedione (2.60 g, 0.03 mole), and the resulting mixture was stirred at room temperature for 24 hr. Anhydrous zinc chloride (4.09 g, 0.03 mole), dissolved in 50 ml of anhydrous methanol, was then filtered by gravity into the stirred dark red-brown solution and the resulting tan crystalline precipitate was collected. In some experiments, a small amount of ether was added to induce crystallization. The tan product was recrystallized from boiling methanol and dried at 78° for 24 hr over P_4O_{10} at reduced pressure; yield, 65%. *Anal.* Calcd for $Ni(C_{10}H_{22}N_4)ZnCl_4$: C, 25.87; H, 4.78; N, 12.07; Cl, 30.5. Found: C, 25.72; H, 4.68; N, 12.02; Cl, 30.70.

Preparation of 2,3-Pentanedionebis(3-aminopropylimino)-nickel(II) Tetrachlorozincate Monohydrate.—This preparation was similar to that described above except that 2,3-pentanedione (3.00 g, 0.03 mole) was introduced instead of 2,3-butanedione and the reaction mixture was stirred for 36 hr at room temperature before adding a methanol solution of zinc chloride. The tan precipitate was recrystallized as described above and dried at room temperature over P_4O_{10} at reduced pressure; yield, 51%. *Anal.* Calcd for $Ni(C_{11}H_{24}N_4)ZnCl_4(H_2O)$: C, 26.62; H, 5.28; N, 11.29; Cl, 28.58. Found: C, 26.78; H, 4.95; N, 11.55; Cl, 28.86.

Preparation of 2,3-Butanedionebis(3-aminopropylimino)nickel-(II) Thiocyanate.—1,3-Diaminopropane (4.44 g, 0.06 mole) was added to a solution prepared by adding $Ni(NO_3)_2 \cdot 6H_2O$ (8.72 g, 0.03 mole) to 450 ml of distilled water. To this solution was added 2,3-butanedione (2.60 g, 0.03 mole) and the solution was stirred at room temperature for 1 hr. This solution was then filtered by gravity to remove a small amount of $Ni(OH)_2$ which had formed during the reaction. The filtrate was saturated with solid sodium thiocyanate and cooled overnight. The crystalline red-brown product was collected and recrystallized from warm methanol and dried at room temperature for 12 hr over P_4O_{10} at reduced pressure. The deuterated sample was prepared by recrystallizing an analytical sample of the complex from deuterium oxide and drying as indicated above; yield, 49%. *Anal.* Calcd for $Ni(C_{10}H_{22}N_4)(NCS)_2$: C, 38.62; H, 5.94; N, 22.52; S, 17.18. Found: C, 38.28; H, 5.94; N, 22.11; S, 16.84.

Preparation of 2,3-Pentanedionebis(3-aminopropylimino)-nickel(II) Thiocyanate.—This complex was prepared by the procedure described above except that 2,3-pentanedione (3.00 g, 0.03 mole) was introduced instead of 2,3-butanedione. Stirring was continued for 3 hr before filtering and only 8 g of sodium thiocyanate was added to the filtrate; yield, 61%. *Anal.* Calcd for $Ni(C_{11}H_{24}N_4)(NCS)_2$: C, 40.32; H, 6.25; N, 21.71; S, 16.56. Found: C, 40.26; H, 6.31; N, 21.54; S, 16.21.

Preparation of 1,2-Cyclohexanedionebis(3-aminopropylimino)-nickel(II) Thiocyanate.—This complex was prepared by the procedure described above except that 1,2-cyclohexanedione (3.36 g, 0.03 mole) was added instead of 2,3-butanedione. The solution was stirred for 8 hr and 10 g of sodium thiocyanate was added. Recrystallization and drying of the red-brown material was performed as indicated above; yield, 55%. Calcd for $Ni(C_{14}H_{24}N_4)(NCS)_2$: C, 42.12; H, 6.06; N, 21.05; S, 16.06. Found: C, 42.21; H, 6.05; N, 21.21; S, 16.01.

Physical Measurements.—Infrared spectra were determined by the potassium bromide pellet and Nujol mull techniques and in chloroform solution with a Perkin-Elmer Model 337 recording spectrophotometer.

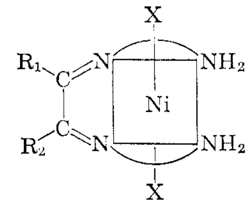
Electronic spectra were obtained with a Cary Model 14 recording spectrophotometer and diffuse reflectance accessory. A magnesium carbonate block was used as the reference material in reflectance measurements. Diffuse transmittance was also employed, using Nujol mulls supported on filter paper.[10]

Magnetic susceptibility data were obtained at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The susceptibilities of ligands and anions were calculated from Pascal's constants.[11]

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Results and Discussion

The reactions of 1,3-diaminopropane with 2,3-butanedione, 2,3-pentanedione, and 1,2-cyclohexanedione proceed smoothly at room temperature over a period of 1–36 hr to yield the complexes represented in III.



III

The complex cations which have been prepared are 2,3-butanedionebis(3-aminopropylimino)nickel(II), 2,3-pentanedionebis(3-aminopropylimino)nickel(II), and 1,2-cyclohexanedionebis(3-aminopropylimino)nickel-(II). These substances are abbreviated as $Ni(BTM)X_2$, $Ni(PTM)X_2$, and $Ni(CTM)X_2$, respectively, where X may be thiocyanate (^-NCS) or tetrachlorozincate ($0.5\ ZnCl_4^{2-}$).

The ligand components are mixed in the presence of nickel(II) ion and allowed to react at room temperature until the solution becomes dark red-brown. The reaction appears to be independent of the concentration of α-diketone or anion, as evidenced by the characteristic color change; however, only thiocyanate and tetrachlorozincate derivatives could be isolated. Substituting ethylenediamine for 1,3-diaminopropane under otherwise identical reaction conditions produced intractable dark brown tars.

The desired Schiff base ligand is unknown in the absence of nickel(II). Attempts were made to prepare this ligand by reaction of 1,3-diaminopropane with the appropriate α-diketone under a variety of conditions, but only orange or red-brown tars were produced. 2,3-Butanedione has previously been shown to react with certain aliphatic polyamines in polar solvents to give infusible tars[12] although similar reactions in benzene with simultaneous removal of water have been shown to yield substituted naphthylpiperazines.[13] These earlier investigators did not study the specific reaction of 1,3-diaminopropane with α-diketones.

The solid complexes $Ni(BTM)ZnCl_4$, Ni(BTM)-

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[10] R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

[11] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

[12] V. V. Korshak and S. V. Vinogradova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, 925 (1955); *Chem. Abstr.*, **50**, 9325g (1956).

[13] H. Stetter, *Chem. Ber.*, **86**, 69 (1953).

$(NCS)_2$, Ni(PTM)$ZnCl_4$, Ni(PTM)$(NCS)_2$, and Ni(CTM)$(NCS)_2$ are precipitated from the reaction medium as red-brown microcrystalline materials. The $ZnCl_4^{2-}$ derivatives are soluble in methanol, nitromethane, dimethylformamide, pyridine, and water (with decomposition of $ZnCl_4^{2-}$). The ^{-}NCS derivatives are soluble in methanol, chloroform, dimethylformamide, and pyridine, the solution being red-brown in each case. The complexes decompose upon contact with either dilute acid or base. Analyses for four elements have established the compositions of the complexes.

The infrared spectra of all of the complexes are closely similar, except for the presence in the spectrum of NiL$(NCS)_2$ of bands which have been attributed to coordinated thiocyanate.[14] The nature of the ligand has been inferred by a comparison of Nujol infrared spectra of the newly prepared complexes and of bis(1,3-diaminopropane)nickel(II) (Table I). Bands in the 3200-cm^{-1} region and at 1598 cm^{-1} have been assigned to the N-H stretching and to NH_2 deformation modes, respectively, of the coordinated amine groups. These assignments have been verified by deuteration experiments After complete deuteration, bands still remain at 1650 and 1590 cm^{-1}. These are probably due to asymmetric and symmetric stretching vibrations of the carbon–nitrogen double bonds (Figure 1). Considering only the metal atom, the two primary nitrogen donors and the two carbon–nitrogen double bonds, the complexes I should have C_{2v} symmetry. Using this point group, symmetry arguments predict two infrared-active C=N stretching frequencies of A_1 and B_2 symmetry.[15] Similar behavior has been observed in the infrared spectra of other N=CC=N-containing compounds such as tris(glyoxalbis(methylimine))nickel(II),[14,16] tris(2,3-butanedionebis(methylimine))nickel(II),[14,16,17] and bis(dimethylglyoximato)-nickel(II).[18]

The infrared spectra of the thiocyanate derivatives have bands at 2062 and 2083 cm^{-1} which have been attributed to the carbon–nitrogen stretching vibration of coordinated thiocyanate.[19,20] Just as two C=N stretching modes were predicted for the Schiff base ligand, there should be an asymmetric and a symmetric C≡N stretching mode for the two thiocyanates. For a *trans* arrangement of the anions only the asymmetric mode should be infrared active while both modes should be infrared active for a *cis* structure. One might easily conclude that the thiocyanates occupy *cis* positions in these complexes on the basis of the two observed vibrational modes in the Nujol mull spectrum, but this splitting could also arise as a result of a nonequivalence in the anion sites associated with packing in the unit cell of the solid. The latter explanation can be ruled out if two bands are observed in the infrared spectrum of the undissociated complex in solution. The infrared spectra of these complexes dissolved in chloroform show only one sharp peak at 2083 cm^{-1}. The assignment of the *trans* structure is not secure on this basis alone, for the coupling of the N≡C frequencies may be very small. However, recognition of the stereochemistry of chelation of these ligands provides strong support for this suggestion.

TABLE I

INFRARED SPECTRA (cm^{-1}) OF Ni(BTM)$(NCS)_2$ AND $NiTm_2(NCS)_2$[a,b]

Ni(BTM)$(NCS)_2$[d]	Assignment	$NiTm_2(NCS)_2$[c,d]
3311 s	N—H str	3307 s
3236 s	N—H str	3300 s
3145 m	N—H str	3257 s
...	N—H str	3170 m
2083 vs	C≡N str	2107 w
2062 vs	C≡N str	2077 vs
...	C≡N str	2031 w
1650 w	C=N str	...
1595 s	N—H def	1597 m
...	N—H def	1588 m
1582 s	C=N str	...

[a] Nujol mulls. [b] Bands due to Nujol have been omitted. [c] N. F. Curtis and Y. M. Curtis, *Australian J. Chem.*, **19**, 1423 (1966). [d] Abbreviations used: s, strong; m, medium; w, weak; v, very; BTM, 2,3-butanedionebis(3-aminopropylimine); Tm, 1,3-diaminopropane.

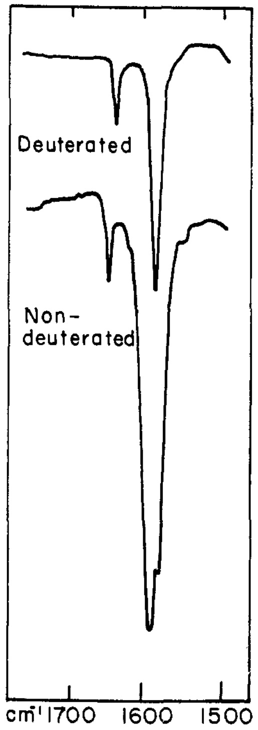

Figure 1.—Nujol infrared spectra of deuterated and nondeuterated Ni(BTM)$(NCS)_2$.

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(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(15) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963.

(16) K. Nakamoto, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 437.

(17) P. E. Figgis and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).

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(19) N. F. Curtis and Y. M. Curtis, *Australian J. Chem.*, **19**, 1423 (1966).

(20) P. C. H. Mitchell and R. G. P. Williams, *J. Chem. Soc.*, 1912 (1960); J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961); F. Basolo, J. L. Burmeister, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 1700 (1963); M. E. Fargo and J. M. James, *Inorg. Chem.*, **4**, 1706 (1965).

TABLE II
MAGNETIC PROPERTIES OF THE NICKEL(II) COMPLEXES AT ROOM TEMPERATURE

Compound	Temp, °K	$10^6\chi_m$	μ_{eff}, BM
$Ni(BTM)ZnCl_4$	302	3962	3.12
$Ni(BTM)(NCS)_2$	300	3900	3.07
$Ni(PTM)ZnCl_4(H_2O)$	301	3699	3.01
$Ni(PTM)(NCS)_2$	301	3894	3.08
$Ni(CTM)(NCS)_2$	299	3947	3.08

Two possible *cis* isomers can be visualized for the present case. In one of these, the α isomer, the primary amine functions of the tetradentate ligand would be mutually *trans*. In this case the *cis*-thiocyanate groups would occupy coordination sites that are identical. The second *cis* form, the β isomer, would place the NCS groups in distinctly different environments. The presence of the α-diimine function in the structure makes the α-*cis* isomer unlikely. Consequently, we expect the β-*cis* form and we expect this isomer to exhibit an infrared spectrum containing two C≡N stretching frequencies. The sharp singlet observed in $CHCl_3$ solutions therefore suggests the *trans* structure.

The carbon–sulfur stretching mode has been used to determine whether the thiocyanate is N or S bonded to the nickel(II). The frequency of the C–S band has been reported to lie in the 690–710-cm^{-1} region for S-bonded complexes and in the range 780–860 cm^{-1} for N-bonded complexes.[19,20] Although the C–S stretching frequency cannot be assigned unequivocally, the bands additional to those observed for the $ZnCl_4^{2-}$ derivatives were always in the range 780–860 cm^{-1}. Therefore, the infrared data lend support to I with *trans*-N-bonded thiocyanates.

Magnetic susceptibility data for those complexes support the proposed structure (Table II). The measured magnetic moments fall in the range 3.01–3.12 BM, lending support to the proposed six-coordinate nature of the nickel ion in the solid state.[11] These values are generally typical of spin-free octahedral nickel(II) complexes.

Electronic spectra were measured in solution and in the solid state, using powders and Nujol mulls. All spectra have band maxima at essentially the same positions except for the lowest energy band. Extinction coefficients obtained from solution spectra are in the range usually seen for octahedral nickel(II).[21] Parity-allowed transitions obscure ν_3 and ν_5 in the spectra of the thiocyanate derivatives. The water molecule in $Ni(PTM)ZnCl_4(H_2O)$ is apparently not coordinated to the nickel ion since the spectra of this material and of $Ni(BTM)ZnCl_4$ are identical.

Although the complexes approximate C_{2v} symmetry, their spectra may be interpreted as though the metal ion were in a tetragonally distorted octahedral site. The interpretation of the visible spectra follows that applied by Wentworth and Piper[22] for cobalt(III) and chromium(III) systems and later applied by several other workers for nickel(II) systems.[23–27] The band maxima presented in Table III are assigned to the following transitions: ν_1, $^3E_g{}^a \leftarrow {}^3B_{1g}$; ν_2, $^3B_{2g} \leftarrow {}^3B_{1g}$; ν_3, $^1A_{1g}$, $^1B_{1g} \leftarrow {}^3B_{1g}$; ν_4, $^3E_g{}^b$, $^3A_{2g}(F) \leftarrow {}^3B_{1g}$; ν_5, ^3E_g, $^3A_{2g}(P) \leftarrow {}^3B_{1g}$. The transition to $^3B_{2g}$ has been shown to be a measure of the in-plane ligand field splitting parameter (Dq^{xy}) and should be approximately constant while the remaining low-energy transition

TABLE III
ELECTRONIC SPECTRA (CM^{-1}) OF THE NICKEL(II) COMPLEXES[a]

Compound	Solvent	ν_1	ν_2	ν_3	ν_4	ν_5
$Ni(BTM)ZnCl_4$	Powder	7,250	12,190	14,280	20,000	25,310
	DMF	8,930 (5.1)	12,350 (3.3)	...	19,230 (34.1)	...
$Ni(BTM)(NCS)_2$	$CHCl_3$	10,750 (13.5)	12,350 (8.1)	...	19,420 (32.6)	...
	Nujol mull	10,630	12,350	...	19,420	...
	CH_3OH	10,180 (8.8)	12,380 (5.6)	...	19,610 (32.5)	...
	Powder	10,750	12,200	...	19,230	...
$Ni(PTM)ZnCl_4(H_2O)$	Powder	7,360	12,340	14,280	20,410	25,640
	DMF	8,930 (5.2)	12,210 (3.3)	...	18,830 (37.2)	...
$Ni(PTM)(NCS)_2$	$CHCl_3$	10,700 (13.0)	12,200 (7.3)	...	19,230 (29.9)	...
	Nujol mull	10,750	12,350	...	19,050	...
	CH_3OH	10,150 (9.0)	12,380 (5.4)	...	19,610 (32.5)	...
	Powder	10,870	12,350	...	19,050	...
$Ni(CTM)(NCS)_2$	$CHCl_3$	10,700 (12.5)	12,200 (9.2)	...	19,230 (36.0)	...
	Nujol mull	10,530	12,200	...	19,050	...
	CH_3OH	10,100 (9.6)	12,420 (6.0)	...	19,420 (36.2)	...
	Powder	10,530	12,050	...	18,870	...

[a] Numbers in parentheses are molar extinction coefficients.

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(21) D. H. Busch, *J. Chem. Educ.*, **41**, 77 (1964).

(22) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(23) G. R. Brubaker and D. H. Busch, *ibid.*, **5**, 2114 (1966).

(24) J. L. Karn and D. H. Busch, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

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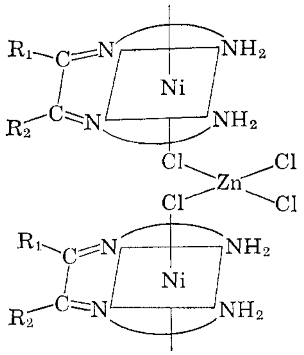
(26) A. B. P. Lever, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 430.

(27) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).

may be used to calculate the ligand field strength of the axial groups (Dq^z) by the relation[22-26]

$$Dq^z = (2\nu_1 - 10Dq^{xy})/10$$

The spectra appear to be consistent with the above model. The transition to $^3B_{2g}$ is essentially constant as would be predicted if the complexes have the same structure in solution as in the solid state. A value of 1228 (average of all ν_2 bands) is quite reasonable for Dq^{xy} since tris(ethylenediamine)nickel(II) and tris(1,10-phenanthroline)nickel(II) have Dq values of 1120 and 1270, respectively.[28] Values of Dq^z for $ZnCl_4^{2-}$ and NCS^- in these complexes have been calculated using the equation given above. A Dq^z value of 220 for $ZnCl_4^{2-}$ was found. This very low Dq value is not too surprising in view of the fact that the chlorides are serving as bridges



The Dq^z value for NCS^- of 920 is in good agreement with Dq^z values for NCS^- obtained with other in-plane ligands containing similar nitrogen donors.[25]

Acknowledgment.—This investigation was supported in part by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences. The assistance of Mr. Ron Lewis in this investigation is gratefully acknowledged.

[28] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

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Complexes Derived from Strong-Field Ligands. XXI. Nickel(II) Complexes of N-Substituted β-Mercaptoethylamines

BY CHARLES A. ROOT AND DARYLE H. BUSCH

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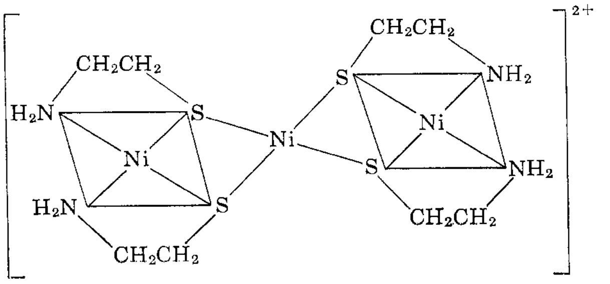
The nickel(II) complexes of ten N- and N,N-disubstituted β-mercaptoethylamines have been prepared and characterized. All are strong-field ligands, producing low-spin, four-coordinate nickel(II). Four classes of complex have been found, and the species produced in a given system is dependent on steric considerations and the reaction conditions. All ligands studied except N,N-diethyl-β-mercaptoethylamine and N-*t*-butyl-β-mercaptoethylamine form the monomeric *trans*-planar complexes NiL_2. The latter two ligands bind through sulfur alone, forming diamagnetic planar complexes that exist as insoluble polymers. Ligands of limited steric requirements form the trinuclear, sulfur-bridged cations $Ni[NiL_2]_2^{2+}$. Highly hindered ligands can form only the dimers $Ni_2L_2X_2$.

Introduction

β-Mercaptoethylamine (MEA) forms two classes of complexes with nickel(II)—planar, diamagnetic $Ni(MEA)_2$ and the trinuclear complex $Ni[Ni(MEA)_2]_2^{2+}$ which also contains only diamagnetic nickel(II) (structure I).[1] A crystal structure[2] shows the presence of three planar nickel(II) atoms, held in the trinuclear ion by sulfur bridges. The trinuclear complex has been prepared by reaction of bis(β-mercaptoethylamine)nickel(II)

$$2Ni(MEA)_2 + Ni^{2+} \longrightarrow Ni[Ni(MEA)_2]_2^{2+} \qquad (1)$$



I

Similar complexes containing various other metal ions in the center metal ion site have been prepared[3] by the reaction of $Ni(MEA)_2$ with different metal salts, *i.e.*, $M[Ni(MEA)_2]_2^{n+}$, where M^{n+} = Cu^+, Cu^{2+}, Pd^{2+}, Pt^{2+}, and Cd^{2+}. Bis(β-mercaptoethylamine)palladium(II) reacts in an analogous fashion and $Ni[Pd(MEA)_2]_2^{2+}$ has been prepared. Related bridged complexes are formed by tris(β-mercaptoethylamine)cobalt(III),[4] but in this case triple bridges are formed, producing sulfur-bonded octahedral nickel(II) in $Ni[Co(MEA)_3]_2^{2+}$.

Bis(β-mercaptoethylamine)nickel(II) has only very limited solubility in polar solvents, and its structure

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[1] D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

[2] L. Dahl, paper presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[3] D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 878 (1962).

[4] D. H. Busch and D. C. Jicha, *ibid.*, **1**, 884 (1962).