

the excited state of the trans isomer and the ground state of the cis isomer. This mechanism which would destabilize the affected levels has been suggested to rationalize the substantial blue shift of the charge-transfer transition observed when going from the *trans*- to *cis*-[Ru(NH₃)₄(py)₂]²⁺.²⁵ It is interesting to compare the ultraviolet spectra of the azide complexes to those of the corresponding nitro complexes. It appears that the $\sigma_L \rightarrow e_g^*$ transition energies are ~ 800 cm⁻¹ higher in energy for the azide complexes.^{8,12} Considering the weaker ligand field of N₃⁻ the opposite

trend would be expected. However the presence of an azide-to-metal charge-transfer absorption in this region²⁸ may give rise to apparent band shifts. In fact, the ultraviolet spectra for the azide complexes are considerably broader and less well defined than for the nitro complexes.

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(25) A. M. Zwicker and C. Creutz, *Inorg. Chem.*, **10**, 2395 (1971).

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Complexes of Binucleating Ligands. V. Some Copper(II) and Nickel(II) Complexes of Two Related Sulfur-Containing Ligands

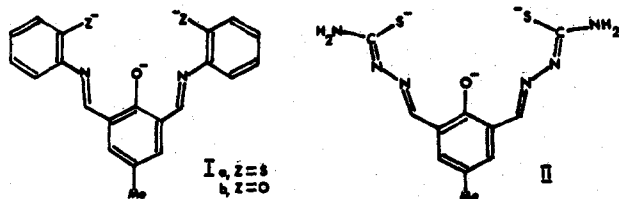
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The synthesis and some properties are described of an extensive series of binuclear copper(II) and nickel(II) complexes derived from the two sulfur-containing binucleating ligands 2-hydroxy-5-methylisophthalaldehyde di-2'-mercaptoanil and 2-hydroxy-5-methylisophthalaldehyde dithiosemicarbazone (derived trianions hereafter represented as L³⁻ and Q³⁻, respectively). The complexes have the general form LM₂X or QM₂X, where X represents a range of monoanionic species incorporated at an accessible bridging site built into the complexes; examples are quoted where X⁻ = OH⁻, 1/2O²⁻, RO⁻, RS⁻, NH₂⁻, NHR⁻, NR₂⁻, C₆H₅N₃⁻, *i.e.* pyrazolate anion, N₃⁻, NCO⁻, and Cl⁻.

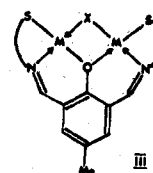
Introduction

The results presented here form part of a long-term project directed toward the synthesis and study of complexes of binucleating ligands¹ designed to bind two metal ions in close proximity. One aspect of this work, to which we are devoting considerable attention, concerns the potential capacity of complexes of appropriately designed binucleating ligands to trap and possibly, in some cases, to activate a range of anionic and neutral species at an in-built accessible bridging site between the two metallic centers. These studies have now been extended to binucleating ligands containing sulfur donor atoms in the hope that they might show enhanced affinity, compared with analogous ligands containing nitrogen and oxygen donor atoms, for "soft" cations, in particular those of the second and third transition series. Reported here are preliminary model studies on some nickel(II) and copper(II) complexes of two trianionic ligands, Ia (hereafter



L³⁻), formally derived from 2-hydroxy-5-methylisophthalaldehyde di-2'-mercaptoanil, and II (hereafter

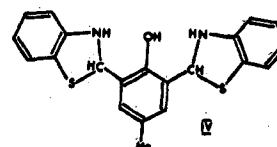
Q³⁻), derived from 2-hydroxy-5-methylisophthalaldehyde dithiosemicarbazone. The primary purpose of these model studies was to determine whether the ligands did indeed impose the desired binuclear arrangement(III) and, if so, to study the gross stereo-



chemical features of the complexes and the range of groups, X⁻, which could be accommodated at the bridging site.

Results and Discussion

Ligands.—Condensation of *o*-aminobenzenethiol with 2-hydroxy-5-methylisophthalaldehyde in ethanol yielded colorless, 2,6-di(2'-benzothiazolanyl)-*p*-cresol (IV) (hereafter LH₃), rather than the di-Schiff base



related to Ia which would be expected to be deeply colored, *e.g.*, 2-hydroxy-5-methylisophthalaldehyde di-2'-hydroxyanil (hereafter referred to as RH₃ where the

(1) R. Robson, *Inorg. Nucl. Chem. Lett.*, **6**, 125 (1970).

TABLE I
ANALYTICAL DATA

	% C		% H		% N		% S		% metal	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
LCu ₂ (OCH ₃)	49.5	49.2	3.4	3.4	5.3	5.2	12.0	11.7	23.8	23.6
LCu ₂ (OC ₂ H ₅)	50.4	50.5	3.7	3.7	5.1	5.1	11.7	11.3	23.2	23.2
LCu ₂ (OCH ₂ C ₆ H ₅)	55.0	55.0	4.0	4.0	4.6	4.7	10.5	10.3	20.8	20.5
LCu ₂ (OH)	48.6	48.6	3.2	3.1	5.4	5.4	12.3	12.0	24.4	24.5
(LCu ₂) ₂ (O)	49.3	49.3	3.0	3.7	5.5	5.2	12.5	12.9	24.9	24.7
LCu ₂ (C ₃ H ₃ N ₂) ^a	50.6	50.3	3.2	3.1	9.8	9.7	11.3	10.9	22.3	22.2
LCu ₂ (N ₃)	46.3	46.2	2.8	2.9	12.9	12.8	11.8	11.7	23.4	23.0
LNi ₂ (OCH ₃)	50.4	50.5	3.5	3.5	5.4	5.4	12.2	12.1	22.4	22.5
LNi ₂ (OC ₂ H ₅)	51.3	51.3	3.8	3.9	5.2	5.2	11.9	11.8	21.8	21.8
LNi ₂ (OCH ₂ C ₆ H ₅)	55.8	56.1	4.0	3.7	4.7	4.6	10.7	10.8	19.5	19.8
LNi ₂ (OH)·DMF	49.4	49.6	4.0	4.0	7.2	7.0	11.0	11.3	20.2	20.7
LNi ₂ (SC ₆ H ₄ CH ₃)	54.5	54.3	3.6	3.6	4.5	4.7	15.6	15.7	19.1	18.9
LNi ₂ (NH ₂)	49.5	49.3	3.4	3.2	8.3	8.1	12.6	12.8	23.1	23.3
LNi ₂ (NHCH ₂ C ₆ H ₅)	56.0	55.7	3.8	3.8	7.0	6.8	10.7	10.4	19.7	19.6
LNi ₂ (NH- <i>n</i> -C ₄ H ₉)	53.1	53.5	4.5	4.4	7.4	7.6	11.4	11.1	20.8	20.8
LNi ₂ (NC ₄ H ₉)DMSO ^b	50.6	50.6	4.6	4.5	6.6	6.5	15.0	14.6	18.4	18.7
LNi ₂ (C ₃ H ₃ N ₂) ^a	51.5	51.5	3.2	3.4	10.0	9.7	11.5	11.5	21.0	21.2
LNi ₂ (N ₃)	47.1	47.4	2.8	3.1	13.1	13.0	12.0	12.1	22.0	22.1
QCu ₂ (OCH ₃)·2DMF	35.4	35.3	4.6	4.5	18.3	18.2	10.5	10.5	20.8	20.6
QCu ₂ (OC ₂ H ₅)·2DMF	36.5	36.8	4.8	5.0	17.9	17.6	10.4	10.2	20.3	20.2
QCu ₂ (OC ₂ H ₄ OCH ₃)	32.9	32.5	3.6	3.5	16.5	16.3	12.6	12.4	24.9	24.8
QCu ₂ (C ₃ H ₃ N ₂) ^a	33.6	33.8	2.9	3.0	22.4	22.0	12.8	12.8	25.4	25.5
QCu ₂ (Cl)·2DMSO ^d	28.8	28.4	3.7	3.7	13.4	13.2	20.4	20.2	20.3	20.3
QCu ₂ (N ₃)·DMSO	28.1	28.0	3.1	3.0	22.7	22.4	17.3	17.0	22.9	23.2
QNi ₂ (OCH ₃)·2DMF	35.9	35.5	4.7	4.5	18.6	18.2	10.7	10.7	19.6	19.9
QNi ₂ (OC ₂ H ₅)·2DMF	37.0	36.9	4.9	4.9	18.2	18.0	10.4	10.1	19.1	19.0
QNi ₂ (OC ₂ H ₄ OCH ₃)	33.6	33.0	3.6	3.2	16.8	16.9	12.8	12.7	23.5	23.7
QNi ₂ (OH)·3DMF ^c	36.2	36.3	5.0	4.9	19.0	18.8	9.6	9.6	17.8	17.7
QNi ₂ (NH ₂)·DMF	32.7	33.0	3.9	3.9	21.8	21.7	12.5	12.5	22.9	23.0
QNi ₂ (NH- <i>n</i> -C ₄ H ₉)·DMF	36.2	36.6	4.3	4.4	19.7	19.4	12.9	12.8	23.6	23.3
QNi ₂ (NHNHC ₆ H ₅)	38.2	38.6	3.6	3.6	21.0	21.4	12.1	12.2	22.0	22.1
QNi ₂ (C ₃ H ₃ N ₂) ^a	34.1	33.9	2.9	2.8	22.8	22.3	13.0	12.8	23.9	24.1
QNi ₂ (SC ₆ H ₄ CH ₃)·2DMF	41.5	41.1	4.7	4.6	16.1	16.1	13.9	14.1	16.9	17.2
QNi ₂ (N ₃)·DMF	31.2	31.5	3.4	3.7	25.9	25.1	11.8	11.5	21.8	21.5
QNi ₂ (NCO)·DMF	33.4	33.4	3.3	3.3	20.7	20.1	11.9	11.9	21.7	21.7
QNi ₂ (Cl)·4DMSO ^e	29.6	29.6	4.6	4.6	10.9	10.9	24.9	25.0	15.3	15.2
QNi ₂ (Cl)·2DMSO ^f	29.2	29.2	3.8	3.7	13.6	13.5	20.8	20.4	19.0	19.4
QNi ₂ (Cl) ^g	28.7	28.4	2.4	2.3	18.3	18.0	13.9	14.1	25.5	25.4

^a C₃H₃N₂⁻ = conjugate base of pyrazole. ^b NC₄H₉⁻ = conjugate base of pyrrolidine. ^c Observed composition also consistent with (QNi₂)₂(O)·6DMF. ^d % Cl: calcd 5.7; found 6.0. ^e % Cl: calcd 4.6; found 4.6. ^f % Cl: calcd 5.8; found 5.8. ^g % Cl: calcd 7.7; found 7.6.

derived trianion, R³⁻, has structure Ib) is deep red in color.² The formation of benzothiazolines rather than Schiff bases by condensation of aldehydes and *o*-aminobenzenethiol has been reported previously.³ Ir spectral evidence supports formulation IV. The neutral Schiff base related to Ia would be expected to show an S-H stretching band in the 2600-cm⁻¹ region of the ir spectrum but no N-H stretching bands, while the isomeric form IV should show N-H stretching bands but no S-H stretching bands. The latter features are in fact observed; two intense N-H stretching bands appear at 3350 and 3250 cm⁻¹ superimposed on a broad band centered near 2900 cm⁻¹ ascribed to the phenolic O-H stretching frequency, consistent with one thiazoline residue hydrogen bonded to the adjacent phenolic group (e.g., 2-(2'-hydroxyphenyl)benzothiazoline shows an N-H stretching band at 3268 cm⁻¹ ^{3c}) and the other thiazoline N-H group free (e.g., 2-(2'-chlorophenyl)benzothiazoline shows an N-H stretching band at 3356 cm⁻¹ ^{3c}). It has previously been observed that benzothiazolines can, in the presence of metal ions and base, yield complexes of the tautomeric Schiff bases⁴

and, likewise, IV proved to be a satisfactory source of L³⁻ in the preparation of complexes.

2-Hydroxy-5-methylisophthalaldehyde dithiosemicarbazone (hereafter QH₃) was prepared by condensation of 2-hydroxy-5-methylisophthalaldehyde with thiosemicarbazide in aqueous ethanol. The carbonyl stretching frequency of the aldehyde (1680 cm⁻¹) and the primary amine bending mode⁵ (1648 cm⁻¹) of the hydrazine fragment of thiosemicarbazide had disappeared in the ir spectrum of the condensation product, and a broad band at 1610 cm⁻¹ probably includes the imine C=N stretching frequency and NH bending modes. There is some disagreement in the literature upon the assignment of ir spectra of thiosemicarbazones,⁶ but the apparently most reliable work^{6b} assigns a medium to strong band in the 840-815-cm⁻¹ range to an almost pure C=S stretching mode. On this basis, a band of medium intensity at 828 cm⁻¹ in the spectrum of QH₃ is assigned to ν_{C=S}.

General Features of Complexes.—The copper(II) and nickel(II) complexes listed in Table I, all of which were either brown or red-brown, were obtained either

(2) R. Robson, *Aust. J. Chem.*, **23**, 2217 (1970).
 (3) (a) J. M. Sprague and A. H. Land, *Heterocycl. Compounds*, **8**, 677 (1967); (b) R. G. Charles and H. Freiser, *J. Org. Chem.*, **18**, 422 (1953); (c) F. J. Goetz, *J. Heterocycl. Chem.*, **4**, 80 (1967); **5**, 501, 509 (1968).

(4) L. F. Lindoy and S. E. Livingston, *Inorg. Chim. Acta*, **1**, 365 (1967).
 (5) M. Mashima, *Bull. Chem. Soc. Jap.*, **37**, 974 (1964).
 (6) (a) N. V. Gerbeleu, *Zh. Neorg. Khim.*, **13**, 2467 (1968); (b) D. M. Wiles and T. Suprunchuk, *Can. J. Chem.*, **45**, 2258 (1967).

by reaction of LH_3 or QH_3 with the metal carboxylate in the presence of a source of the bridging species X^- or by exchange of one bridging group for another. In many cases attempted recrystallization led to decomposition, and it was generally necessary to adjust the reaction conditions so that the complexes crystallized directly from the reaction mixture in a pure form. With few exceptions, complexes of L crystallized in an unsolvated form, but those of Q were generally solvated with either DMF or DMSO. In some cases, attempted desolvation of the latter by heating under vacuum led to general decomposition, but in other cases analytically pure solvent-free residues could be obtained. All residues so obtained, except $QNi_2(Cl) \cdot 2DMSO$ and $QNi_2(Cl)$, apparently differed on the basis of spectra and magnetism from the parent materials in only a trivial manner and are not discussed here.

On the basis of the evidence given below all the complexes with the possible exceptions of $QNi_2(C_3H_3N_2)$ and $QCu_2(C_3H_3N_2)$ are assigned structures of the basic type III. In the particular case of $QNi_2(OC_2H_5) \cdot 2DMF$, this was unambiguously established by single-crystal X-ray diffraction studies⁷ which revealed that the DMF molecules were neither coordinated to nickel nor hydrogen bonded to the ligand and that all the atoms (other than hydrogen) in the complex molecule were coplanar except for the methyl carbon atom of the ethoxide bridge.

In most cases molecular weight determination by osmometry was precluded by insufficient solubility, but in the five cases amenable to such studies which are quoted in Table II the observed molecular weights

TABLE II
MOLECULAR WEIGHTS BY OSMOMETRY

Complex	Found	Theoret	Solvent
$LNi_2(N_3)$	534	535	Pyridine
$LNi_2(C_3H_3N_2)$	579	560	Pyridine
$LNi_2(NH-n-C_4H_9)$	579	565	Chloroform
$LCu_2(N_3)$	533	545	Pyridine
$QNi_2(C_3H_3N_2)$	531	492	Pyridine

provided good support for structures of the type III. In all the solutions used for molecular weight determinations the solutes behaved as nonelectrolytes.

Ir spectra, although very complex, support the general conclusion that a particular binucleating ligand assumes much the same coordination mode and geometry in all the complexes reported here (with the possible exception, discussed below, of Q in its pyrazole derivatives). In the spectra of each of the series of complexes, LM_2X and QM_2X , a common basic pattern of peaks could be discerned; however, in both series minor differences between the spectra of the copper complexes and the nickel complexes were apparent. Additional bands due to solvent molecules or the bridging X groups, some examples of which are discussed below, could be located in many cases. The availability of a large number of related complexes derived from the same binucleating ligand and also of many groups of complexes with the same bridging group but derived from different binucleating ligands was particularly useful in this respect, affording some confidence in the assignment of peaks either to the

binucleating ligand or to the bridging group. The positions of bands due to ν_{CO} of DMF (1640–1670 cm^{-1}) or ν_{SO} of DMSO (1010–1040 cm^{-1}) did not allow a decision as to whether these solvent molecules were coordinated, hydrogen bonded, or in lattice sites. No attempt has been made to assign metal-ligand stretching frequencies because of the general complexity of the spectra in this region. The common bands (cm^{-1}) in the spectra (2000–500 cm^{-1}) of the LNi_2X series were as follows: 1612 ± 3 (w) (aromatic skeletal in-plane vibration), 1575 ± 3 (m), 1535 ± 5 (s), 1462 ± 3 (s), 1380 (m), 1346 ± 4 (m) (phenolic C–O stretching frequency), 1296 ± 4 (w), 1262 ± 2 (w), 1242 ± 2 (m), 1188 ± 3 (m), 1155 ± 5 (w), 1138 ± 3 (vw), 1103 ± 5 (s), 1074 ± 4 (w), 1038 ± 2 (w), 1006 ± 4 (vw), 934 ± 6 (w), 804 ± 10 (w), 743 ± 3 (s) (C–H out-of-plane deformation of ortho-disubstituted benzene ring), 712 ± 3 (m), 565 ± 5 (m), 520 ± 10 (w). The most marked difference between the LNi_2X and LCu_2X spectra was the splitting of the $1575\text{-}cm^{-1}$ band of the former into a resolved doublet, 1590 and $1575\text{-}cm^{-1}$, in the latter. Other differences include the shifting of the strong 1103 ± 5 to $1086 \pm 2\text{-}cm^{-1}$ in the LCu_2X series and the intensification of bands at ~ 1612 , ~ 1380 , and $\sim 840\text{-}cm^{-1}$. In all cases within the L series the $1535 \pm 2\text{-}cm^{-1}$ band was the strongest in the $1500\text{--}1620\text{-}cm^{-1}$ region and, in some cases, the strongest in the entire spectrum. LH_3 itself shows a band of medium intensity at $1585\text{-}cm^{-1}$ (probably N–H bending of the thiazoline superimposed on an aromatic skeletal in-plane vibration) and a weak band at $1610\text{-}cm^{-1}$ (aromatic skeletal in-plane) but, significantly, shows no other absorption in this region down to beyond $1500\text{-}cm^{-1}$. Since absorption in this region due purely to vibrations within the aromatic systems might reasonably be expected to be not drastically different in LH_3 as compared with the L complexes (except perhaps for some intensification of the $\sim 1580\text{-}cm^{-1}$ band resulting from conjugation within L^{3-}), we are driven to the consideration that the very intense band at $1535 \pm 2\text{-}cm^{-1}$ is in some way associated with the imine linkage despite the unusually low value if this is what is often referred to as "the" C=N stretching frequency.⁹ Dudek and Dudek¹⁰ have concluded, on the basis of shifts in the ir spectra of some Schiff base complexes resulting from ^{15}N substitution, that the concept of group frequencies is inadequate in such cases. We propose therefore, that the absorptions at ~ 1535 and $\sim 1575\text{-}cm^{-1}$ are related to vibrations involving more than two nuclei but that both are intimately associated with the imine link. The significant differences in this region between the spectra of the LCu_2X and LNi_2X series probably reflect nothing more than different degrees of axial interaction between a metal atom of one binuclear complex with a ligand atom (S or, less likely, O) of an adjacent molecule in the crystal. Most likely such interaction is negligible in the LNi_2X series (as is definitely the case in QNi_2 -

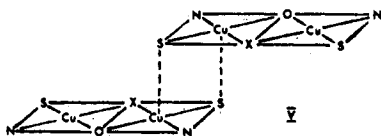
(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p 72.

(9) B. Das Sarma and J. C. Bailar, *J. Amer. Chem. Soc.*, **77**, 5476 (1955); C. S. Marvel, S. A. Aspey, and E. A. Dudley, *ibid.*, **78**, 4905 (1956); P. Teyssie and J. J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963); B. Das Sarma, K. R. Ray, R. E. Seivers, and J. C. Bailar, *J. Amer. Chem. Soc.*, **86**, 14 (1964); E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem.*, **26**, 1582 (1964); C. M. Harris and E. D. McKenzie, *J. Chem. Soc. A*, 746 (1969).

(10) E. P. Dudek and G. Dudek, *Inorg. Nucl. Chem. Lett.*, **3**, 241 (1967).

(7) B. F. Hoskins, H. Schaap, and R. Robson, *Inorg. Nucl. Chem. Lett.*, in press.

(OC₂H₅)₂·2DMF⁷) but is significant in the LCu₂X series. The splitting of the ~1575-cm⁻¹ band in the latter case may then arise from axial interactions as in V, rendering the two side arms of a particular ligand



no longer equivalent. This sort of tetranuclear association definitely exists in the closely related RCu₂(C₃H₃N₂).¹¹

The ir spectra of the Q complexes showed generally much broader bands and poorer resolution than those of the L series but much the same picture emerges. In the N-H stretching region a broad band of medium intensity appears in the range 3100-3170 cm⁻¹ in all the spectra, and one or more generally broad and unresolved bands appear at higher frequency. The following bands (cm⁻¹) in the 2000-500-cm⁻¹ range are common to the QNi₂X derivatives: 1615 ± 15 (s) (often obscured in the DMF solvates by the ν_{CO} band of the DMF), 1573 ± 3 (w), 1550 ± 5 (w), 1510 ± 10 (vs) (NH bending), 1451 ± 6 (w), 1370 ± 10 (m), 1330 ± 5 (s) (phenolic C-O stretching frequency), 1233 ± 4 (m), 1185 ± 5 (w), 1155 ± 10 (w-m), 920 ± 10 (w-m), 855 ± 5 (w), 795 ± 8 (w), 752 ± 8 (m), 622 ± 8 (m). Again, while the ir spectra of the QCu₂X series were in most respects very similar to those of the QNi₂X series, minor differences were apparent; e.g., the pair of weak bands at 1573 ± 3 and 1550 ± 5 cm⁻¹ in QNi₂X were shifted to 1588 ± 8 and 1545 ± 5 cm⁻¹, the very strong band at 1510 ± 10 cm⁻¹ was shifted to 1487 ± 13 cm⁻¹, and the medium band at 622 ± 8 cm⁻¹ was shifted to 600 ± 10 cm⁻¹ in QCu₂X. As discussed above, these differences probably reflect more pronounced axial interactions in the copper series. The spectra of QNi₂(C₃H₃N₂) and QCu₂(C₃H₃N₂) were somewhat atypical and receive further discussion below.

Because of intense absorption bands centered at higher energies but tailing into the region where d-d bands might have been expected, no bands of the latter origin could be detected in either the diffuse reflectance or (where possible) the solution spectra of the complexes.

The general magnetic behavior of the complexes provided further support for the proposed binuclear structures. All except those quoted in Table III were effectively diamagnetic. The magnetic behavior of the two paramagnetic nickel complexes is discussed below. The variation of the molar susceptibility per metal atom with temperature of LCu₂(C₃H₃N₂), QCu₂(C₃H₃N₂), QCu₂(N₃)·DMSO, and QCu₂(Cl)·2DMSO is given in Figure 1 in which is also indicated the agreement between the experimental observations and the χ_M vs. T (°K) curves calculated on the basis of the Bleaney-Bowers equation¹² for antiferromagnetically coupled cupric dimers taking the values for J, g, and TIP indicated in Table III. The agreement, while not providing unambiguous proof of the presence of binuclear units, certainly affords strong support for

TABLE III
PARAMAGNETIC COMPLEXES

Compound	μ _{eff} , ^a BM	Temp, °K	J, ^b cm ⁻¹	g ^b	TIP, ^b cgs
LCu ₂ (C ₃ H ₃ N ₂)	1.2	295	-372	2.0	30
QCu ₂ (C ₃ H ₃ N ₂)	1.2	290	-414	2.2	50
QCu ₂ (N ₃)·DMSO	1.0	287	-472	2.0	20
QCu ₂ (Cl)·2DMSO	1.2	296	-430	2.3	40
LCu ₂ (N ₃)	0.7	293			
QNi ₂ (Cl)·4DMSO	2.0	295			
QNi ₂ (Cl)·2DMSO	1.9	295			

^a μ_{eff} = effective magnetic moment per metal atom, corrected for diamagnetic contributions but not for temperature-independent paramagnetism (TIP). ^b Values taken to yield the agreement indicated in Figure 1 between experimental data and data calculated on the basis of the Bleaney-Bowers equation.

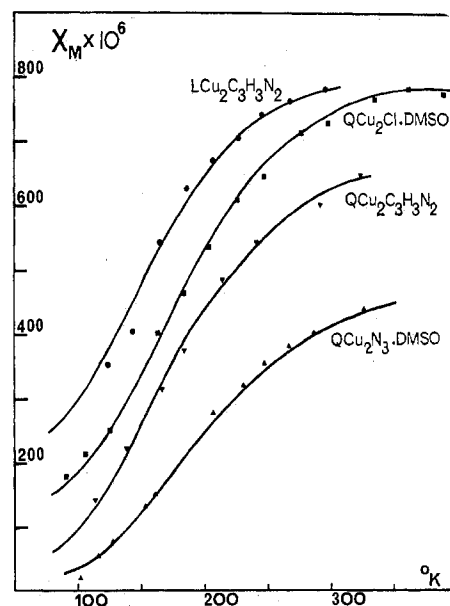


Figure 1.—Plots of molar susceptibility, χ_M, vs. temperature. Full lines represent theoretical curves taking the values for J, g, and TIP indicated in Table III. Theoretical curves and experimental points are raised 100 cgs units for QCu₂Cl·2DMSO and 200 cgs units for LCu₂(C₃H₃N₂) to avoid confusion in the figure. Susceptibilities were corrected for diamagnetism using Pascal's constants.

this proposal. The paramagnetic susceptibility of LCu₂(N₃) was so low as to preclude meaningful curve fitting to theoretical data, but the general behavior (became effectively diamagnetic at 125°K) was consistent with strong antiferromagnetic coupling within pairs of cupric ions as was the effective diamagnetism at room temperature of the remaining cupric complexes. Binuclear cupric complexes which either are diamagnetic at room temperature or become diamagnetic at lower temperatures are not without precedent.¹³

Alkoxides, Hydroxides, Oxides, and Mercaptides.—The alkoxides generally were readily obtained by reaction of either LH₃ or QH₃ with the appropriate metal carboxylate in the presence of the appropriate alcohol or by heating one alkoxy-bridged complex in the presence of an excess of a different alcohol. Elemental analyses and the absence of carboxylate bands or alcohol O-H stretching bands in the ir spectra argue

(11) B. F. Hoskins and D. Vince, unpublished results of a single-crystal X-ray diffraction analysis.

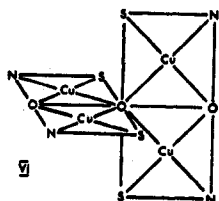
(12) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, **214**, 451 (1952).

(13) C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959); S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer, and E. Sinn, *Aust. J. Chem.*, **20**, 2403 (1967); S. Misumi and K. Koya, *Bull. Chem. Soc. Jap.*, **42**, 2403 (1969).

strongly that the anionic fragment associated with $(LM_2)^+$ or $(QM_2)^+$ was derived from the alcohol despite the fact that all the products reported here, in contrast to most alkoxides, were apparently indefinitely stable in air. The bridging role of the alkoxide was confirmed by X-ray crystallography in the case of $QNi_2(OC_2H_5) \cdot 2DMF^7$ and there can be little doubt that all the other alkoxides, hydroxides, and mercaptides have related structures. We have previously pointed out² that on the basis of molecular models the mere existence, let alone the apparently considerable stability, of alkoxy-bridged binuclear derivatives of R^3- (Ib) is surprising, for the models suggested that in order to achieve "normal" metal-oxygen distances the angle subtended at a metal ion by the alkoxide oxygen and the phenoxide oxygen must be considerably smaller than 90° and that the two bridging oxygen atoms must be very close, perhaps unrealistically so. This structural feature was clearly revealed in the X-ray study of $QNi_2(OC_2H_5) \cdot 2DMF^7$ in which the distance between the two oxygen atoms in question was only 2.38 Å as compared with the sum of the van der Waals radii of ~ 2.8 Å.

$LCu_2(OH)$ and $LNi_2(OH) \cdot DMF$ were obtained by heating the corresponding ethoxides with undried DMF, presumed to contain small quantities of water. The ir spectrum (hexachlorobutadiene mull) of the copper compound showed an O-H stretching vibration of medium intensity at 3493 cm^{-1} which was unusually sharp for a band of this origin. The O-H stretching band of the DMF-solvated nickel complex was considerably broader and at lower energy, 3320 cm^{-1} , which suggests hydrogen bonding, possibly with the DMF in the lattice.

Solutions containing cupric isobutyrate and LH_3 in DMSO upon standing yielded a brown crystalline solid which had an elemental composition consistent with $(LCu_2)_2(O)$ and which showed an ir spectrum almost identical with that of $LCu_2(OH)$ except that the sharp O-H stretching band was totally absent. This compound very probably has the tetranuclear structure VI with an oxide ion bridging four cupric



ions. A crystalline O-H free nickel(II) complex solvated with DMSO with presumably an analogous structure could be obtained in the same way, but the elemental composition while approximating to $(LNi_2)_2(O) \cdot 2DMSO$ was variable.

Solutions containing nickel acetate and QH_3 in hot DMF yielded, upon cooling, a brown crystalline solid with elemental composition consistent with either $QNi_2(OH) \cdot 3DMF$ or $(QNi_2)_2(O) \cdot 6DMF$. Unfortunately in the ir spectrum of this compound the broad ill-resolved absorption due to the N-H stretching vibrations of Q obscured any O-H stretching bands if present.

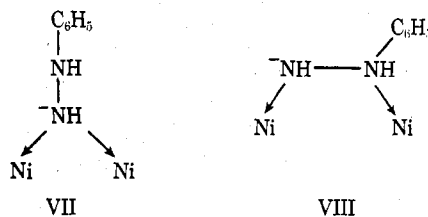
The mercaptides $LNi_2(SC_6H_4CH_3)$ and $QNi_2(SC_6H_4CH_3) \cdot 2DMF$, both presumably having structures

of the type III, were obtained by reaction of the corresponding ethoxides with *p*-thiocresol in DMF.

Amides.—An even more striking example of the apparent ability of the LM_2^+ or QM_2^+ unit to form a stable union with highly basic bridging X^- groups is provided by the amido-bridged complexes. The simple ammonia-derived amide $QNi_2(NH_2) \cdot DMF$ crystallized from reaction mixtures in which the source of NH_2^- was NH_4^+ while acetate ion was the strongest base present; in other words, the extremely powerful base NH_2^- is stabilized by QNi_2^+ so markedly that the weak base acetate ion competes with it successfully for protons. The other amido-bridged complexes were prepared by reaction of the appropriate ethoxide-bridged complex either with ammonium ion or with the appropriate amine. Unlike most amides which are very sensitive to moisture and protic solvents in general,¹⁴ the amides reported here appeared to be unusually stable; *e.g.*, they were all apparently indefinitely stable in air and $LNi_2(NH-n-C_4H_9)$ could be recrystallized from undried DMF and recovered unchanged from refluxing ethanol.

The N-H stretching region of the ir spectra provided useful information in the cases of the L-derived amides, but with the Q complexes absorption by the binucleating ligand obscured any peaks due to the amide bridging group. The observed N-H stretching bands (cm^{-1} , hexachlorobutadiene mull) which were generally very sharp were as follows: $LNi_2(NH_2)$ 3290 (m), 3200 (w); $LNi_2(NHCH_2C_6H_5)$ 3240 (m); $LNi_2(NH-n-C_4H_9)$ 3250 (m). Significantly, the amido-bridged complex derived from the secondary amine pyrrolidine showed no N-H stretching bands, which eliminates any suspicion that the amine fragment was present somehow as the amine rather than its conjugate base. Two N-H stretching frequencies are expected for the $NiNH_2Ni$ system, but it is uncertain whether the observed pair of bands represent symmetric and anti-symmetric stretching frequencies or whether they reflect inequivalence of the two hydrogen atoms in the crystal lattice.

In $QNi_2(NHNHC_6H_5)$ the amido anion may bridge in one of two possible ways, VII and VIII. To our



knowledge this is the first example of the conjugate base of phenylhydrazine behaving as a bridging ligand.

Pyrazolate Derivatives.—In earlier reported work with the binucleating ligand RH_3 , the pyrazolate anion was chosen and studied as a geometrical model for a (as yet) hypothetical mode of nitrogen fixation by strongly reducing binuclear species.² For the same reason the incorporation of pyrazolate into the accessible bridging site of binuclear complexes derived from L and Q has been studied. Pyrazolate derivatives were readily obtained by reaction of the appropriate alkoxide with pyrazole. An X-ray crystallographic study of $RCu_2(C_3H_3N_2)^{11}$ revealed the bridging mode

IX. Comparison of the ir spectrum of this compound



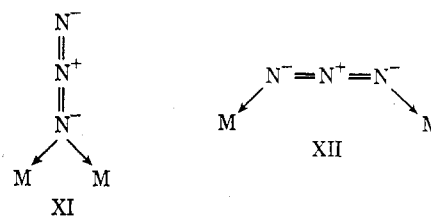
with those of many other complexes of R allowed the identification of the following bands (cm^{-1}) as originating in the pyrazolate bridging system: doublet at 1625 and 1630 (m) (in-plane skeletal vibrations), 1058 (m), 736 (m) (C-H out-of-plane deformation). Similar comparisons in the Q and L series of compounds allow the location of the following bands (cm^{-1}) of presumably related origin in the pyrazolate fragment: $\text{QNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ doublet at 1621 and 1628 (m), 1074 (m), 730 (m); $\text{QNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ 1625 (broad), 1064 (m), 740 (m); $\text{LNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ 1594 (m), 1072 (m), 730- cm^{-1} region obscured by L band; $\text{LCu}_2(\text{C}_3\text{H}_3\text{N}_2)$ 1600 (m), 1064 (m), 735 (sh). These data suggest the bridging mode IX, particularly so in the case of the Q derivatives. However, in the case of the L derivatives, the possibility of bridging through a single nitrogen atom, X, as in the amides discussed above, cannot be entirely discounted since the absorption in the 1600- cm^{-1} region is significantly different from that of $\text{RCu}_2(\text{C}_3\text{H}_3\text{N}_2)$. Some support for this notion is provided by a study of molecular models which suggest that the bulky sulfur donor atoms in L might have the effect of pushing the two metal ions closer together than is the case with R, and consequently mode X may be preferred over mode IX.

Several features of the ir spectra of $\text{QNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ and $\text{QCu}_2(\text{C}_3\text{H}_3\text{N}_2)$, which can be ascribed an origin within Q, set these compounds apart from all the other Q derivatives; e.g., the N-H stretching bands were very much sharper and better resolved ($\text{QNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ 3140 (m), 3320 (m), small shoulders at 3370 and 3280 cm^{-1} ; $\text{QCu}_2(\text{C}_3\text{H}_3\text{N}_2)$ 3160 (m), 3280 (m), 3320 (m), and 3370 (m) cm^{-1}), and the most intense band in all the Q spectra near 1500 cm^{-1} , which is probably associated with NH bending vibrations, appeared at $1510 \pm 10 \text{ cm}^{-1}$ in all the QNi_2X spectra except $\text{QNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ when it was found at 1535 cm^{-1} . Several other bands which consistently appeared in the spectra of all the other Q derivatives were either shifted or absent in the pyrazolates. The differences probably indicate a geometrical arrangement of Q in the pyrazolates significantly different from that found in all the other Q complexes. If, as seems likely, the pyrazolate is incorporated as in IX, the metal ions may be significantly farther apart than in all the other complexes (e.g., the Cu-Cu distance of 3.36 Å in $\text{RCu}_2(\text{C}_3\text{H}_3\text{N}_2)$ ¹¹ is to be compared with the Ni-Ni distance in $\text{QNi}_2(\text{OC}_2\text{H}_5) \cdot 2\text{DMF}$ of only 2.88 Å⁷). This may introduce strain into the thiosemicarbazone side arms when the bulky sulfur atoms act as donors, which may be relieved by distortion of the side arm out of coplanarity, or alternatively N-coordination may become preferred to S-coordination. It is unfortunate that these compounds are too insoluble to allow nmr spectra to be recorded, and it is difficult to conceive how the above uncertainties can be resolved without resort to X-ray

crystallography. Such studies upon $\text{QNi}_2(\text{C}_3\text{H}_3\text{N}_2)$ are at present underway.¹⁵

Azides and Cyanates.—The azide and cyanate derivatives crystallized from reaction mixtures containing LH_3 or QH_3 plus the appropriate metal carboxylate and either sodium azide or sodium cyanate. Attempts to prepare $\text{LNi}_2(\text{NCO})$ yielded materials of variable composition. All attempts to carry out parallel reactions with thiocyanate ion failed to yield thiocyanate-containing products.

The only two known modes of azide bridging involve coordination either through a single nitrogen atom as in XI¹⁶ or through the two terminal nitrogen atoms as in XII.¹⁷ In the azido-bridged complexes reported



here, mode XII seems highly unlikely on steric grounds, requiring the cations to be much further apart than the binucleating ligand can allow and can be excluded on the basis of ir evidence (Table IV) as follows. Nelson

TABLE IV
AZIDE AND CYANATO STRETCHING FREQUENCIES (KBr DISK)

	$\nu_{\text{asym}}, \text{cm}^{-1}$	$\nu_{\text{sym}}, \text{cm}^{-1}$
$\text{LNi}_2(\text{N}_3)$	2090 (s)	1294 (m)
$\text{LCu}_2(\text{N}_3)$	2075 (s)	1270 (m)
$\text{QNi}_2(\text{N}_3) \cdot \text{DMF}$	2090 (s)	1298 (m)
$\text{QCu}_2(\text{N}_3) \cdot \text{DMSO}$	2085 (s)	1280 (m) (sh)
$\text{QNi}_2(\text{NCO}) \cdot \text{DMF}$	2180 (s)	

and Nelson¹⁸ have concluded that while the ν_{asym} azide stretching frequency is of little diagnostic value, ν_{sym} can be used to distinguish between modes XI and XII. These authors report that the appearance of a band of medium intensity near 1300 cm^{-1} , ascribed to ν_{sym} , indicates the presence of bridging azide as in XI, whereas for mode XII, in which the azide fragment is much more symmetrically bound, ν_{sym} is inactive or, at best, very weak. The bands of medium intensity near 1300 cm^{-1} observed in all four azido-bridged complexes reported here strongly support bridging by mode XI.

The ir spectrum of $\text{QNi}_2(\text{NCO}) \cdot \text{DMF}$ (Table IV) is less useful. As with the azides the ν_{asym} cyanate vibrations are of little diagnostic value and the ν_{sym} cyanate band expected in the 1300 cm^{-1} region could not be located. Nelson and Nelson report that the ν_{sym} band of a number of complexes presumed to be bridged through the nitrogen atom of the cyanate ion was generally much weaker than that in the analogous azide-bridged complexes.¹⁸ Bridging by the cyanate in a manner analogous to XII can again be excluded on steric grounds and by analogy with the above azides. While cyanate appears to have a strong preference for

(15) H. Schaap, work in progress.

(16) For example, see W. Beck, H. Englemann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Commun.*, 496 (1971).

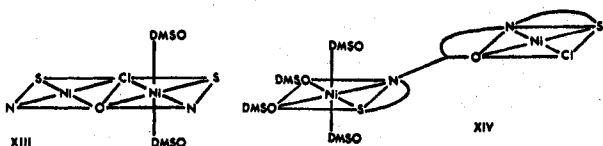
(17) For example, see R. F. Ziola, A. P. Gaughan, Z. Dori, C. G. Pierpoint, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971).

(18) J. Nelson and S. M. Nelson, *J. Chem. Soc. A*, 1597 (1969).

bridging through nitrogen rather than oxygen¹⁸ the available evidence in the present instance does not allow this ambiguity to be resolved.

Chlorides.— $\text{QNi}_2(\text{Cl}) \cdot 4\text{DMSO}$ and $\text{QCu}_2(\text{Cl}) \cdot 2\text{DMSO}$ were readily obtained in pure crystalline form from DMSO solutions containing QH_3 and a mixture of the metal chloride and acetate. Repeated attempts to prepare analogous complexes of L yielded, in the case of copper, impure materials of variable composition approximating to $\text{LCu}_2(\text{Cl}) \cdot \text{DMSO}$ and, in the case of nickel, the presumed oxide referred to above, $(\text{LNi}_2)_2(\text{O}) \cdot 2\text{DMSO}$, in impure form.

$\text{QNi}_2(\text{Cl}) \cdot 4\text{DMSO}$ and the derived $\text{QNi}_2(\text{Cl}) \cdot 2\text{DMSO}$ are the only nickel compounds reported here which are truly paramagnetic. The paramagnetism of $\text{QNi}_2(\text{Cl}) \cdot 4\text{DMSO}$ obeyed the Curie-Weiss law over the temperature range 100–300°K (Figure 2). The room-temperature magnetic moment per nickel atom of 2.0 BM together with the Curie-Weiss behavior is strongly suggestive of equal numbers of nickel cations in the spin singlet and triplet states. The observed susceptibility would then imply a magnetic moment for the paramagnetic center of almost exactly the "spin only" value for a spin triplet. Two ways, XIII and XIV, in which this situation might arise immediately



present themselves, the pseudo-square-planar nickel ion being the diamagnetic center in both cases. Mass loss measurements under vacuum at various temperatures indicated that near 100° two of the four DMSO molecules were rapidly lost while a temperature of 140° was required to remove all the DMSO. In this way residues with elemental compositions consistent with $\text{QNi}_2(\text{Cl}) \cdot 2\text{DMSO}$ and $\text{QNi}_2(\text{Cl})$ could be obtained. Significantly $\text{QNi}_2(\text{Cl})$ was effectively diamagnetic while $\text{QNi}_2(\text{Cl}) \cdot 2\text{DMSO}$ had a magnetic moment of 1.9 BM per nickel atom, little different from that of the parent material. These results strongly suggest XIII rather than XIV for, in the former, the two DMSO molecules removed would be lost from lattice sites leaving the environment of the paramagnetic pseudo-octahedral nickel ion intact; loss of further DMSO would then yield pseudo-square-planar diamagnetic nickel(II). Unfortunately the broad intense ν_{SO} band of DMSO in these complexes throws no light on this question, although the remainder of the ir spectra showing the pattern of bands present in all the other QNi_2X complexes indicates XIII rather than XIV in which Q must adopt a very different geometry. There can be little doubt that $\text{QCu}_2(\text{Cl}) \cdot 2\text{DMSO}$ has the common structure III in view of its magnetic behavior and its ir spectrum (common pattern), and therefore any suspicion that XIV is preferred to XIII in the nickel complexes as a result of excessive strain in XIII introduced by the relatively large chloride bridge can be eliminated.

It is interesting that only one of the two nickel ions takes on DMSO ligands; indeed, we have attempted repeatedly but without success to obtain binuclear complexes derived from nearly planar binucleating

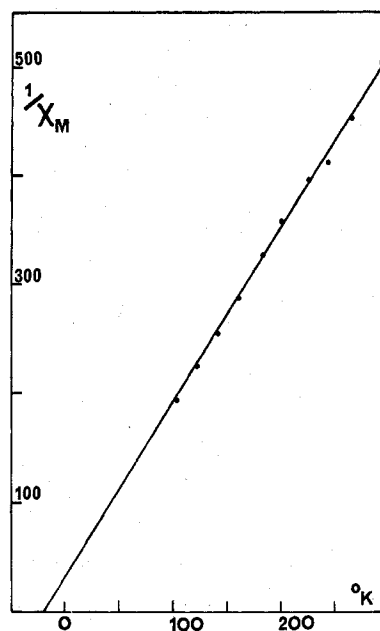


Figure 2.—Plot of reciprocal of molar susceptibility vs. temperature for $\text{QNi}_2(\text{Cl}) \cdot 4\text{DMSO}$. χ_M = molar susceptibility per nickel atom corrected for diamagnetic contributions using Pascal's constants but not for temperature-independent paramagnetism. $\theta = -19^\circ\text{K}$.

ligands such as Q, L, and others in which the two cations each take on an extra two monodentate ligands (e.g., H_2O pyridine, amines), one above and one below the plane of the binucleating ligand. Possibly, in such structures the two monodentate ligands attached on the same side of the binucleating ligand plane to neighboring cations would be in prohibitively close proximity.

Experimental Section

LH₃.—A solution of 25 g of 2-hydroxy-5-methylisophthalaldehyde in 400 ml of ethanol was added to a solution of 83 ml of *o*-aminobenzenethiol in 600 ml of ethanol, and the reaction vessel was stoppered. Upon standing, the product separated as pale yellow crystals, which were collected, washed with ethanol, and dried under vacuum, yield 49.3 g. The ligand LH₃ obtained in this fashion was used, without further purification, in the preparation of complexes. LH₃ was obtained as a white crystalline solid when it was prepared under argon, but this material was virtually identical with that prepared under the above conditions, as indicated by ir and analysis.

Preparation of Complexes.—Because decomposition accompanied attempted recrystallization in most cases, it was necessary to adjust reaction conditions so that pure products crystallized directly from the reaction medium. Many of the procedures that follow are very similar, but essential details for all are included because slight modification of the conditions yielded impure amorphous products in many cases.

LCu₂(OCH₃).—A hot solution of 1.5 g of LH₃ in 340 ml of DMSO was added to a hot solution of 4.35 g of cupric isobutyrate in 340 ml of DMSO and 95 ml of methanol. The intense brown solution deposited brown crystals which were collected, washed successively with methanol and diethyl ether, and dried at 80° under vacuum, yield 1.87 g.

LCu₂(OC₂H₅).—A hot solution of 2 g of LH₃ in 450 ml of DMSO was added to a hot solution of 5.8 g of cupric isobutyrate in 450 ml of DMSO and 125 ml of ethanol. The intense brown solution deposited brown needles which were collected, washed successively with ethanol and diethyl ether, and dried under vacuum at 80°, yield 2.16 g.

LCu₂(OCH₂C₆H₅).—This was prepared in two ways.

(a) A suspension of 0.3 g of $\text{LCu}_2(\text{OC}_2\text{H}_5)$ in 25 ml of DMF and 6 ml of benzyl alcohol was warmed and stirred when a brown crystalline product resulted which was collected, washed with DMF and then diethyl ether, and dried under vacuum at 80°.

(b) Hot solutions of 0.58 g of cupric isobutyrate in 90 ml of DMSO and 30 ml of benzyl alcohol and 0.2 g of LH_3 in 90 ml of DMSO were mixed, and the resultant intense brown solution deposited brown crystals which were collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried at 80° under vacuum.

$\text{LCu}_2(\text{OH})$.—A suspension of 1 g of finely ground $\text{LCu}_2(\text{OC}_2\text{H}_5)$ in 100 ml of DMF (unpurified LR grade presumably containing a small amount of water) was gently warmed and stirred. After several minutes the $\text{LCu}_2(\text{OC}_2\text{H}_5)$ was replaced by very fine brown crystals which were collected, washed successively with DMF and diethyl ether, and dried under vacuum at 80°, yield 0.81 g.

$(\text{LCu}_2)_2(\text{O})$.—A hot solution of 0.2 g of LH_3 in 90 ml of DMSO was added to a hot solution of 0.58 g of cupric isobutyrate in 90 ml of DMSO. The resultant intense brown solution deposited brown crystals which were collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried under vacuum at 80°.

$\text{LCu}_2(\text{C}_3\text{H}_3\text{N}_2)$.—A hot solution of 0.25 g of pyrazole in 10 ml of DMF was added to a suspension of 0.2 g of $\text{LCu}_2(\text{OC}_2\text{H}_5)$ in 10 ml of DMF. Upon warming and stirring an intense brown solution resulted which then deposited fine brown crystals. The product was collected, washed with DMF and then diethyl ether, and dried at 80° under vacuum, yield 0.14 g.

$\text{LCu}_2(\text{N}_3)$.—A hot solution of 3 g of LH_3 in 75 ml of DMSO was added to a hot solution of 6.51 g of cupric isobutyrate and 5.15 g of sodium azide in 225 ml of DMSO. Upon cooling for a few minutes the intense brown solution deposited brown crystals which were collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried under vacuum at 80°, yield 2.18 g.

$\text{LNi}_2(\text{OCH}_3)$.—A suspension of 1.2 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$ in 20 ml of methanol and 100 ml of DMF was warmed and stirred when the $\text{LNi}_2(\text{OC}_2\text{H}_5)$ was replaced by fine brown crystals. The product was collected, washed with methanol, and dried at 80° under vacuum, yield 1.14 g.

$\text{LNi}_2(\text{OC}_2\text{H}_5)$.—A hot solution of 2 g of LH_3 in 450 ml of DMSO was added to a hot solution of 5.3 g of nickel acetate tetrahydrate in 900 ml of ethanol and 450 ml of DMSO. The intense brown solution deposited red-brown needles which were collected, washed with ethanol and diethyl ether, and dried at 80° under vacuum, yield 1.84 g.

$\text{LNi}_2(\text{OCH}_2\text{C}_6\text{H}_5)$.—A suspension of 1 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$ in 100 ml of benzyl alcohol was heated and stirred at 100°, whereupon the $\text{LNi}_2(\text{OC}_2\text{H}_5)$ was replaced by fine red-brown needles. The product was collected, washed with diethyl ether, and dried at 80° under vacuum, yield 1.04 g.

$\text{LNi}_2(\text{OH})\cdot\text{DMF}$.—A suspension of 0.5 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$ in 25 ml of DMF (LR grade, presumed wet) was warmed and stirred, whereupon the $\text{LNi}_2(\text{OC}_2\text{H}_5)$ was replaced by red-brown crystals. The product was collected, washed with diethyl ether, and dried at 80° under vacuum.

$\text{LNi}_2(\text{SC}_6\text{H}_4\text{CH}_3)$.—A suspension of 1 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$ in 100 ml of DMSO, containing a large excess of *p*-thiocresol, was warmed and stirred for 15 hr when the $\text{LNi}_2(\text{OC}_2\text{H}_5)$ was replaced by a red-brown crystalline product, which was collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried at 80° under vacuum.

$\text{LNi}_2(\text{NH}_2)$.—A solution of 1.86 g of nickel acetate tetrahydrate and 0.58 g of ammonium acetate in 100 ml of DMSO was added to 1 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$, and upon warming and stirring the suspended $\text{LNi}_2(\text{OC}_2\text{H}_5)$ was slowly replaced by fine brown crystals. The product was collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried at 80° under vacuum. In an effort to prepare $\text{LNi}_2(\text{NH}_2)$ under the conditions given below, a product resulted in which one $=\text{NC}_6\text{H}_4\text{S}^-$ side arm was replaced by $=\text{N}-\text{H}$, as indicated by elemental composition and the presence in the ir spectrum of bands at 3185 cm^{-1} (m) ($\text{N}-\text{H}$ str) and 1650 cm^{-1} (s) ($\text{C}=\text{N}$ str).

To a hot solution of 0.525 g of nickel acetate tetrahydrate in 25 ml of DMSO (prior to addition of the nickel acetate the DMSO was saturated with gaseous ammonia at room temperature) was added a hot solution of 0.2 g of LH_3 in 25 ml of DMSO. The resultant intense brown solution almost immediately deposited a brown product, which was collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried at 80° under vacuum. *Anal.* Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{SONi}$: C, 55.1; H, 3.7; N, 8.6; S, 9.8; Ni, 18.0. Found: C, 55.4; H, 3.8; N, 8.5; S, 9.8; Ni, 18.4.

$\text{LNi}_2(\text{NHCH}_2\text{C}_6\text{H}_5)$.—To a suspension of 1 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$ in 100 ml of benzene was added 20 ml of benzylamine. Upon gently warming, an intense brown solution resulted, which then deposited brown crystals. The product was collected, washed with benzene and then diethyl ether, and dried at 80° under vacuum, yield 1.07 g.

$\text{LNi}_2(\text{NH}-n-\text{C}_4\text{H}_9)$.—This was prepared in the same way as $\text{LNi}_2(\text{NHCH}_2\text{C}_6\text{H}_5)$, except that *n*-butylamine was used in place of benzylamine, yield 0.88 g.

$\text{LNi}_2(\text{NC}_2\text{H}_5)\cdot\text{DMSO}$.—A solution of 0.93 g of nickel acetate tetrahydrate and 0.75 ml of pyrrolidine in 25 ml of DMSO was added to 0.5 g of solid $\text{LNi}_2(\text{OC}_2\text{H}_5)$. After the mixture was warmed and stirred, an intense brown solution resulted, which deposited brown needles upon standing for 2 days. The product was collected, washed successively with DMSO, *p*-dioxane, and diethyl ether, and dried at 80° under vacuum, yield 0.27 g.

$\text{LNi}_2(\text{C}_3\text{H}_3\text{N}_2)$.—This was prepared in two ways.

(a) A hot solution of 1 g of LH_3 in 100 ml of DMF was added to a hot solution of 2.64 g of nickel acetate tetrahydrate and 0.36 g of pyrazole in 100 ml of DMF. Almost immediately the intense brown solution deposited fine brown needles. The product was collected, washed with DMF and then diethyl ether, and dried at 80° under vacuum.

(b) A solution of 0.43 g of nickel nitrate hexahydrate and 0.10 g of pyrazole in 20 ml of DMF was added to 0.2 g of $\text{LNi}_2(\text{OC}_2\text{H}_5)$. Upon refluxing for a few minutes the $\text{LNi}_2(\text{OC}_2\text{H}_5)$ dissolved to give an intense brown solution, which on cooling deposited brown needles. The product was collected, washed with DMF and diethyl ether, and dried at 80° under vacuum.

$\text{LNi}_2(\text{N}_3)$.—Hot solutions of 2.63 g of nickel acetate tetrahydrate in 75 ml of DMSO and 1.38 g of sodium azide in 75 ml of methanol were mixed, and to the resultant solution was added a hot solution of 1 g of LH_3 in 50 ml of DMSO. The resultant intense brown solution deposited fine brown needles which were collected and washed successively with DMSO, *p*-dioxane, and diethyl ether and dried at 80° under vacuum; yield 1.25 g.

QH_3 .—A hot solution of 2-hydroxy-5-methylisophthalaldehyde (4.84 g) in ethanol (500 ml) was added to a hot solution of thiosemicarbazide (7.34 g) in water (200 ml). On cooling, the yellow solution yielded pale yellow crystals, which were collected, washed with ethanol, and dried under vacuum at 60°, yield 9.1 g. *Anal.* Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$: C, 42.6; H, 4.5; N, 27.1; O, 5.2; S, 20.7. Found: C, 42.8; H, 4.8; N, 26.6; O, 5.6; S, 19.7. The product in this form was satisfactory for the preparation of complexes, but could be recrystallized from a mixture of DMF and ethanol.

$\text{QCu}_2(\text{OCH}_3)\cdot 2\text{DMF}$.—A hot solution of the ligand QH_3 (0.3 g) in DMF (20 ml) and methanol (20 ml) was added to a hot solution of copper acetate monohydrate (0.5 g) in DMF (15 ml) and methanol (10 ml). On cooling, the dark brown solution yielded dark brown plates, which were collected, washed with a little DMF, and dried under vacuum at room temperature.

$\text{QCu}_2(\text{OC}_2\text{H}_5)\cdot 2\text{DMF}$.—A solution of the ligand QH_3 (1.3 g) in DMF (970 ml) and ethanol (970 ml) at 90° was slowly added to a solution of copper isobutyrate (1.68 g) in DMF (480 ml) at 35°. The initial noncrystalline product dissolved on heating the solution to its boiling point. The hot solution was then filtered, cooled, and allowed to stand for 24 hr, when brown plates formed, which were collected, washed with DMF and then ethanol, and quickly dried under vacuum at 80°.

$\text{QCu}_2(\text{OC}_2\text{H}_5\text{OCH}_3)$.—By suspending finely powdered $\text{QCu}_2(\text{OC}_2\text{H}_5)\cdot 2\text{DMF}$ in a hot solution of 1:1 DMF-2-methoxyethanol for 2 hr, the complex $\text{QCu}_2(\text{OC}_2\text{H}_5\text{OCH}_3)$ was obtained as a brown amorphous powder. The compound was washed with DMF and dried at 80° under vacuum.

$\text{QCu}_2(\text{C}_3\text{H}_3\text{N}_2)$.—The compound $\text{QCu}_2(\text{OC}_2\text{H}_5)\cdot 2\text{DMF}$ (0.1 g) was suspended in hot DMF (3 ml), to which was added a solution of pyrazole (0.06 g) in DMF (1 ml). After heating with constant stirring for 30 min, the crystalline product was collected, washed with DMF, and dried at 80° under vacuum.

$\text{QCu}_2(\text{Cl})\cdot 2\text{DMSO}$.—A hot solution of the ligand (3.1 g) in DMSO (80 ml) was added to a hot solution of copper acetate monohydrate (3.0 g) and cupric chloride dihydrate (1.7 g) in DMSO (120 ml). The dark brown solution which formed was filtered while hot and allowed to cool to room temperature. After 2 days at room temperature, dark brown crystals separated, which were collected, washed with a small volume of DMSO, and dried at room temperature under vacuum for 2 days.

$\text{QCu}_2(\text{N}_3)\cdot\text{DMSO}$.—Copper isobutyrate (3.5 g) and sodium azide (1.0 g) were dissolved in DMSO (30 ml) and the ligand

QH₃ (1.5 g) was separately dissolved in DMSO (10 ml). Both solutions were heated to 90°, filtered, and combined with constant stirring. On cooling, brown, needlelike crystals formed which were collected by filtration, washed with DMSO, and dried at room temperature under vacuum for 3 days.

QNi₂(OCH₃)₂·2DMF.—A hot solution of the ligand (0.31 g) in DMF (20 ml) and methanol (20 ml) was added to a hot solution of nickel acetate tetrahydrate (0.5 g) in DMF (15 ml) and methanol (10 ml). The deep brown solution was quickly filtered and allowed to cool to room temperature when dark brown crystals precipitated. The crystals were collected, washed with a small volume of cold DMF, and dried under vacuum at room temperature for 13 hr.

QNi₂(OC₂H₅)₂·2DMF.—A solution of the ligand QH₃ (2.7 g) in DMF (500 ml) and ethanol (500 ml) was heated to 90°. Nickel acetate tetrahydrate (9.4 g) was dissolved in DMF (500 ml) on heating to 90°; the solution was then filtered, ethanol (500 ml) added, and the mixture heated to 90°. The two solutions were combined, yielding a dark brown solution, from which dark brown plates separated on standing after 24 hr. The crystals were collected and washed, first with DMF-ethanol solution, followed by ethanol, and dried under vacuum at 80° for 6 hr.

QNi₂(OC₂H₄OCH₃)₂.—The complex was prepared in the same way as the copper analog by using QNi₂(OC₂H₅)₂·2DMF as the starting reagent.

QNi₂(OH)₂·3DMF or (QNi₂)₂(O)₂·6DMF.—A solution of the ligand (0.31 g) in hot DMF (80 ml) was added to a hot solution of nickel acetate tetrahydrate (0.75 g) in DMF (100 ml). On cooling, the initial amorphous precipitate was filtered off and discarded. Brown crystals formed when the filtrate was allowed to stand for several days. The crystals were filtered off, washed with DMF, and dried at room temperature under vacuum.

QNi₂(C₃H₃N₂)₂.—This compound was prepared in the same way as the corresponding copper complex, but using QNi₂(OC₂H₅)₂·2DMF as the starting material.

QNi₂(NH₂)₂·DMF.—The complex was prepared in two ways.

(a) A solution at 90° of QH₃ (0.31 g) and ammonium acetate (0.25 g) in DMF (80 ml) was added to a solution of nickel acetate tetrahydrate (0.75 g) in DMF (100 ml) at 90°. A small quantity of amorphous precipitate was filtered from the hot solution which was then allowed to cool for 24 hr, whereupon brown crystals separated. The solid was collected, washed with DMF, and dried under vacuum at room temperature for 10 hr.

(b) A solution of the ligand (0.31 g) in hot DMF (100 ml) was combined with a solution of nickel acetate tetrahydrate (0.5 g) in DMF (130 ml). To the somewhat turbid solution, 0.880 M ammonium solution (0.34 ml) was added dropwise whereupon the solution became clear. The hot, dark red-brown solution was filtered and allowed to cool to room temperature when crystals separated. After filtration and washing, the crystals were dried at 70° under vacuum for 6 hr.

QNi₂(NH-*n*-C₄H₉)₂·DMF.—The complex QNi₂(OC₂H₅)₂·2DMF was dissolved in a minimum volume of hot 1:25 *n*-butylamine-DMF. The dark red-brown solution was filtered hot, and on cooling, dark red needles formed, which were collected by filtration, washed with a small volume of DMF, and dried at 70° under vacuum.

QNi₂(NHNHC₆H₅)₂.—This compound was prepared in the same way as QNi₂(NH-*n*-C₄H₉)₂·DMF, except that phenylhydrazine was used instead of *n*-butylamine.

QNi₂(SC₆H₄CH₃)₂·2DMF.—To a suspension of finely powdered QNi₂(OC₂H₅)₂·2DMF in hot DMF, an excess of *p*-thiocresol in hot DMF was added. The resulting mixture was heated until all solid dissolved. The dark brown solution was filtered hot and allowed to cool to room temperature when crystals separated. The crystals were collected, washed with DMF, and dried at room temperature under vacuum for 24 hr.

QNi₂(N₃)₂·DMF.—A hot solution of the ligand (0.31 g) and sodium azide (0.16 g) in DMF (100 ml) was added to a solution of nickel acetate tetrahydrate (0.37 g) and nickel perchlorate hexahydrate (0.28 g) in DMF (100 ml) at 100°. The resulting hot solution was filtered and allowed to cool to room temperature over a period of 24 hr when a brown crystalline solid separated. The crystals were collected, washed with a little solvent, and dried at room temperature under vacuum.

QNi₂(NCO)₂·DMF.—A solution of the ligand (0.31 g) and sodium cyanate (0.1 g) in DMF (60 ml) was heated to 90° and slowly added to a solution of nickel acetate tetrahydrate (0.37 g) and nickel perchlorate hexahydrate (0.28 g) in DMF (75 ml). A dark brown solution formed which was allowed to cool to 0° and allowed to stand for 10 days. A small quantity of crystalline solid separated, which was washed with DMF and dried at room temperature under vacuum.

QNi₂(Cl)₂·*x*DMSO (*x* = 4, 2, 0).—A solution of the ligand (3.1 g) in DMSO (60 ml) at 90° was added to a solution of nickel acetate tetrahydrate (3.73 g) and nickel chloride hexahydrate (1.58 g) in hot DMSO (100 ml). The dark brown solution was filtered and allowed to cool to room temperature. Crystals of QNi₂(Cl)₂·4DMSO formed on standing for 4 days at 20° (a better yield was obtained if the solution was frozen and then allowed to warm to room temperature). The crystals were collected, washed, and then dried to constant weight under vacuum at 25° for several days. The compound QNi₂Cl₂·2DMSO was obtained by drying the crystals at 110° under vacuum for 24 hr, while QNi₂(Cl)₂ formed on drying crystals at 140° under vacuum for several days.

Physical Measurements.—Spectra were recorded using the following instruments: ir spectra on a Perkin-Elmer 457 grating spectrophotometer; electronic spectra on a Beckman DK-2A spectrophotometer. Ir frequencies quoted in this paper refer to KBr disks unless otherwise indicated. Magnetic moments were measured by the Gouy method using mercury cobalt(II) tetrathiocyanate as calibrant. Conductance measurements were made using a Philips PR 9500 bridge. Molecular weights were determined using a Hitachi Perkin-Elmer Model 115 apparatus.

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