mentioned it was noted in this work that $AgCNS{\cdot}P(n\text{-}Bu)_3$ decomposed in the presence of benzene.

As is well known the thiocyanate ion in metal ion complexes can coordinate through the sulfur atom or through the nitrogen atom or can act as a bridging group using both atoms. Infrared criteria for establishing the bonding mode based on frequency ranges observed for three vibrational modes of the thiocyanate ion have been published by Burmeister[12] and others. The Burmeister ranges are given as footnotes to Table II.

If the CN stretch criterion alone were applied to the infrared data obtained for the new silver thiocyanate complexes reported in this paper (Table II), it would be concluded that $AgCNS{\cdot}PEt_2Ph$, $AgCNS{\cdot}P(n\text{-}Bu)_3$, and possibly $AgCNS{\cdot}PMe_3$ were S bonded and that the remaining complexes were N bonded. However, application of the CS stretch criterion where data could be obtained would indicate bridge bonding for all the 1:1 and 1:2 complexes. Support for the presence of bridge bonding in the 1:1 complexes is provided in a report of an X-ray crystallographic study by Panattoni and Frasson[5] of the related compound $AgCNS{\cdot}P(n\text{-}Pr)_3$. This trialkylphosphine complex contains zigzag polymeric -Ag-SCN-Ag-SCN- chains cross-linked in pairs by Ag-S bonds to form double chains having a stair-step configuration. The reported silver-nitrogen bond distance of 2.10 ± 0.10 Å corresponds to the calculated covalent value but the silver-sulfur bond lengths of 2.83 ± 0.02 and 2.88 ± 0.02 Å are substantially longer than the calculated single-bond covalent value of 2.56 Å. The above was considered to be consistent with a CN stretching frequency of 2090 cm^{-1} in the nitrogen-bonding range.

Pending the acquisition of X-ray structure data it thus seems reasonable to assume that the 1:1 complexes prepared in this work also form double-chain structures. The CN stretching frequency shift from one complex to another might then be interpreted as indicating the relative Ag-N and Ag-S bond strengths within the double chain.

The 1:2 complexes prepared in this work probably all have dimeric structures involving a central $(AgSCN)_2$ ring with a quasiplanar structure. This prediction is based on conclusions from X-ray study on $AgSCN{\cdot}2PPh_3$.[13] The bridging role of the thiocyanate group within the dimer is consistent with CS stretching vibration values and as with the 1:1 complexes the CN stretch values could be tentatively considered to reflect the relative Ag-N and Ag-S bond strengths.

It is of particular interest to note that complexes of both 1:1 and 1:2 stoichiometries were formed with diethylphenylphosphine. It will be noted further that the 1:1 complex has a CN stretching frequency that is 45 cm^{-1} greater than the 1:2 complex indicating a substantially greater relative sulfur bond strength in the 1:1 complex. The synthesis of these compounds seem to be at least a partial fulfillment of the prediction by Turco and Pecile,[4] that in compounds of the type $M(CNS)_mX_n$ a change in the m:n ratio might change the bonding mode of the thiocyanate group. This phenomenon of ligand-multiplicity linkage isomerism has apparently been observed previously with the complexes of bis(diphenylphosphino)acetylene with gold(I), $(DPPA)Au_2(SCN)_2$ (believed to be S bonded) and $(DPPA)_3Au_2(NCS)_2$ (believed to be N bonded).[14,15]

Table II. Infrared Data (cm^{-1})

Compd	ν(C-N)[a]	ν(C-S)[b]	δ(N-C-S)
$AgCNS{\cdot}PEt_2Ph$	2128 vs, 2075 sh	*c*	450 m, 441 m
$AgCNS{\cdot}P(i\text{-}Pr)_3$[d]	2111 s	738 m	475 s
$AgCNS{\cdot}P(n\text{-}Bu)_3$	2108 vs, 2068 sh	*c*	454 w, 444 w
$AgCNS{\cdot}PMe_3$	2100 s, 2050 sh	757 m	456 w, 447 w
$AgCNS{\cdot}2PPh_3$	2092 vs, 2050 sh	*c*	484 m
$AgCNS{\cdot}2PCy_3$[d]	2090 s	732 w	462 s
$AgCNS{\cdot}P(n\text{-}Pr)_3$[d]	2090 s	*c*	*c*
$AgCNS{\cdot}2SbPh_3$	2084 vs	754 w	*c*
$AgCNS{\cdot}2PEt_2Ph$	2083 s	*c*	494 m
$AgCNS{\cdot}2AsPh_3$	2082 vs	*c*	478 m
$AgCNS{\cdot}3PEtPh_2$	2074 vs	*c*	*c*

[a] M-SCN, $\gtrsim$2100; M-NCS, $\lesssim$2100; M-NCS-M, $\gtrsim$2140. [b] M-SCN, 690-720; M-NCS, 780-860; M-NCS-M, 720-780. [c] Masked by ligand absorptions. [d] C. Pecile, *et al., Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, 28, 189 (1960).

As previously mentioned the 1:3 stoichiometry observed with ethyldiphenylphosphine is somewhat surprising in view of the 1:2 stoichiometries observed with both diethylphenyl- and triphenylphosphine. With three ligands in addition to the thiocyanate group coordinated to the silver it is likely that this complex is a monomer and the low CN stretch value of 2074 cm^{-1} seems to be a definite indication of Ag-N bonding.

Registry No. $AgCNS{\cdot}PMe_3$, 38744-31-9; $AgCNS{\cdot}PBu_3$, 38744-32-0; $AgCNS{\cdot}PEt_3$, 38744-33-1; $AgCNS{\cdot}2PEt_2Ph$, 38671-58-8; $AgCNS{\cdot}3PPh_2Et$, 38731-29-2; $AgCNS{\cdot}2PPh_3$, 36470-96-9; $AgCNS{\cdot}2AsPh_3$, 38671-60-2; $AgCNS{\cdot}2SbPh_3$, 38671-61-3.

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[12] J. L. Burmeister, *Coord. Chem. Rev.*, 3, 225 (1968).

[13] J. Howatson and B. Morosin, *Cryst. Struct. Commun.*, 2, 51 (1973).

[14] A. J. Carty and A. Efraty, *Inorg. Chem.*, 8, 543 (1969).

[15] N. J. DeStefano and J. L. Burmeister, *Inorg. Chem.*, 10, 998 (1971).

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Absence of Selectivity in the Synthesis and Equilibration of $[Co(en)_2(S\text{-}glu)]^+$ Ions

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It has been reported[1,2] that treatment of an aqueous solution of racemic $[Co(en)_2CO_3]ClO_4$ with (*S*)-(+)-glutamic acid at elevated temperatures (steam bath or 100°) results in the initial formation of Λ-(+)$[Co(en)_2(S\text{-}glu)]^+$ followed by the slower formation of an equal amount[3] of the Δ-*S* dia-

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[1] J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1966).

[2] J. H. Dunlop, R. D. Gillard, and N. C. Payne, *J. Chem. Soc. A*, 1469 (1967).

[3] R. D. Gillard, N. C. Payne, and G. B. Robertson, *J. Chem. Soc. A*, 2579 (1970).

stereoisomer. Other workers reported a final product distribution of 70% Λ-*S* and 30% Δ-*S* forms of $[Co(en)_2(S\text{-glu})]^+$ when the reaction is carried out in the presence of activated charcoal.[4] The reported kinetic selectivity was surprising to us and during the course of other investigations we have had cause to repeat both sets of experiments. In this note we give results which demonstrate the lack of kinetic and thermodynamic preference in the reaction.

Experimental Section

Treatment of $[Co(en)_2CO_3]ClO_4$ (3.4 g) with (*S*)-(+)-glutamic acid (Fluka Puriss, $[\alpha]^{20}{}_{546}$ +36 ± 2°, 1.48 g) in water (50 ml) at steam bath temperatures resulted in the isolation of Λ-(+)$[Co(en)_2(S\text{-glu})]$-$(ClO_4)\cdot H_2O$ ($[\alpha]_{589}$ 295°; $[\alpha]_{546}$ 683°) as the least soluble product[2] (solution pH 6–6.5). Alternatively sorption of the product solution on Dowex 50W-X2 (200–400 mesh) cation-exchange resin and elution with 1 *M* HCl (or $NaClO_4$) resulted in the separation of five bands of which the second (in order of elution) was shown to be $[Co(en)_2(S\text{-glu})]^{2+}$ and the fourth $[Co(en)_3]^{3+}$. The $[Co(en)_2(S\text{-glu})]^{2+}$ fraction (30–50% total cobalt) was reduced to dryness, taken up in water, neutralized to pH 5 with LiOH, and converted to the perchlorate salt using Bio-Rad AG1-X8 (200–400 mesh) anion-exchange resin (ClO_4^- form). Reduction of the eluent volume and treatment with $LiClO_4$ resulted in crystallization of Λ-(+)$[Co(en)_2(S\text{-glu})](ClO_4)\cdot H_2O$, identical with that obtained directly from the reaction mixture. *Anal.* Calcd for $Co(C_9H_{23}N_5O_4)ClO_4\cdot H_2O$: C, 24.47; H, 5.70; N, 15.85; Co, 13.34. Found: C, 24.8; H, 5.7; N, 15.70; Co, 13.3 (ϵ_{489}(max) 104, ϵ_{340}(max) 118 (in H_2O or 1 *M* $NaClO_4$)). The Δ-*S* isomer was not obtained as a crystalline salt. A portion of the eluted $[Co(en)_2(S\text{-glu})]Cl_2$ fraction was neutralized (pH 5) with NaOH and sorbed on a longer (80 cm) column of Dowex 50W-X2 resin (200–400 mesh, Na^+ form). The Λ-*S* and Δ-*S* diastereoisomers were separated by elution with 0.2 *M* $NaClO_4$; the Λ-*S* isomer eluted first. The two bands were collected, their visible and rotatory dispersion spectra recorded, and their concentrations determined by atomic absorption spectroscopy for cobalt (ϵ_{489}(max) 104, ϵ_{340}(max) 118 for both isomers; $[\alpha]_{589}$ 297° (Λ-*S*), −350° (Δ-*S*)). The diastereoisomers were also separated using the following conditions: Dowex 50W-X4 (200–400 or 100–200 mesh, Na^+ form), 0.2 *M* $NaClO_4$; Dowex 50W-X4 (200–400 mesh, Na^+ form), 0.5 *M* HCl; SE or CM-Sephadex C-25 (Na^+ form), 0.05 *M* $NaClO_4$ or HCl. The eluent was recycled using a peristaltic pump, and once the bands had separated, the eluent was changed to HCl and the Λ- and Δ-$[Co(en)_2(S\text{-glu})]Cl_2$ salts were recovered.

Preparations in the presence of Norit A activated charcoal[4] gave higher yields (>80%) of ΔΛ-$[Co(en)_2(S\text{-glu})]^{2+}$, but the relative amounts and physical properties (visible, rotatory dispersion, and pmr (100 MHz) spectra) of the separated Λ-*S* and Δ-*S* isomers were the same as those obtained previously.

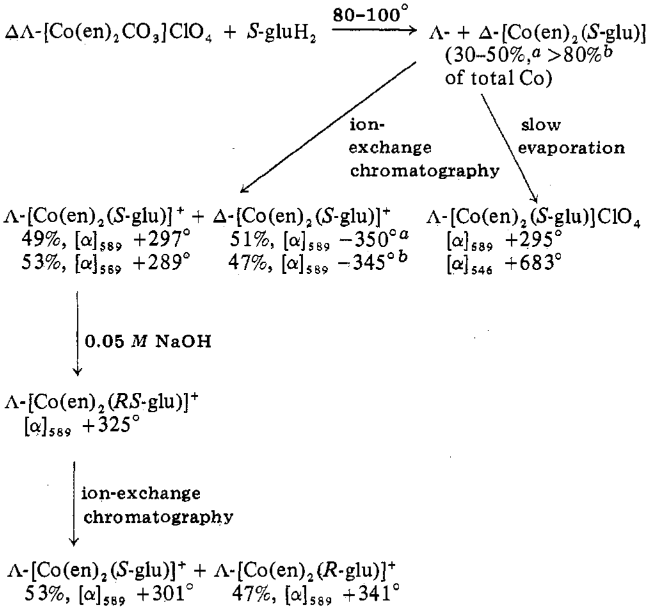
A similar reaction to the above was carried out using Δ-(−)D-$[Co(en)_2CO_3]ClO_4\cdot 0.5H_2O$ ([α]D −1340°). The rotation and visible spectrum of the $[Co(en)_2(S\text{-glu})]^{2+}$ band obtained after elution with 1 *M* HCl was measured ($[\alpha]_{589}$ −22°). Also, the racemization of Δ-(−)D$[Co(en)_2(OH)(H_2O)]^{2+}$, prepared by treating the active carbonato complex with 2 equiv of $HClO_4$, was followed on the polarimeter at 430 nm in collidine buffer (0.2 *M*), pH 6.22, 25°. The half-life was 6.6 min.

Product Analyses at Time Intervals. The following experiments were carried out to investigate the proposed kinetic selectivity.[1,2] A solution (400 ml) of $[Co(en)_2CO_3](ClO_4)$ (3.38 g) and (*S*)-glutamic acid (1.47 g) was heated under reflux, and 60-ml samples were removed at the time intervals given in Table I. Rotations at 589, 546, and 450 nm were measured (∿0.1% solutions, 1-dm cell, Perkin-Elmer P-22 polarimeter, 25°). The solutions were then separately sorbed on Dowex 50W-X2 cation-exchange resin (H^+ form), eluted with 1.5 *N* HCl, and the $[Co(en)_2(S\text{-glu})]^{2+}$ bands were collected. The fractions were concentrated on a rotatory evaporator at 20° to give finally ∿0.1% solutions in water and their rotations measured (Table I). The amount of $[Co(en)_2(S\text{-glu})]^{2+}$ recovered maximized after 1–2 hr after which it steadily decreased and the solution turned yellow-brown. At least six products were observed at shorter times; after 495 min the major product was $[Co(en)_3]^{3+}$.

Table I. Measured Rotations (∿0.1% Solutions) during Reaction of $[Co(en)_2CO_3]ClO_4$ and (*S*)-(+)-Glutamic Acid in Aqueous Solution at 100°

Time, min	Solution α_{546}, deg	Solution α_{589}, deg	No. of products	$[Co(en)_2glu]^+$ α_{546}, deg
15	−0.010	+0.003	8	+0.005
30	+0.015	+0.006	8	+0.003
65	+0.005	+0.007	6	+0.007
120	+0.008	−0.007	6	+0.002
240	−0.003	+0.003	5	−0.003
495			3	

Scheme I



[a] Conditions as described in ref 2. [b] Conditions as described in ref 4.

Mutarotation Experiment. To an aqueous solution of Λ-$[Co(en)_2(S\text{-glu})]ClO_4\cdot H_2O$ (10 mg in 5 ml of H_2O, [α]D 295°) was added 5 ml of 0.1 *M* NaOH (μ = 1.0, $NaClO_4$). The change in optical activity (∿0.08°) was followed at 450 nm (P-22 polarimeter, 1-dm cell, 25°). Plots of log $(\alpha_\infty - \alpha_t)$ *vs.* time were linear over 3 half-lives and duplicate experiments gave $k_{\text{obsd}} = 8.1 \times 10^{-4}$ sec^{-1}. The final solutions were sorbed on Dowex 50W-X2 resin (200–400 mesh) and eluted with 0.2 *M* $NaClO_4$, pH ∿4. The two $[Co(en)_2(glu)]^+$ bands were eluted and concentrated by rotatory evaporation, and the rotations, visible spectra, and cobalt concentrations (atomic absorption) of the solutions were measured.

Results and Discussion

The previously reported[1,2] isolation of Λ-$[Co(en)_2(S\text{-glu})]$-ClO_4 from the preparative solution resulting from treating racemic $[Co(en)_2CO_3]ClO_4$ with (*S*)-glutamic acid has been confirmed. However, the results given in Table I demonstrate the low optical activity of both the solution and the isolated $[Co(en)_2(S\text{-glu})]^{2+}$ fractions during the course of the reaction. This result requires the absence of kinetic selectivity; the isolation of the Λ-*S* isomer only reflects the solubility relationship between the diastereoisomers. Furthermore, a similar preparation using Δ-$[Co(en)_2CO_3]ClO_4$ gave equal amounts of Δ- and Λ-$[Co(en)_2(S\text{-glu})]^+$. Since both the Λ-*S* and Δ-*S* isomers are stable to mutarotation under the conditions, this result requires racemization to occur prior to their formation and it was demonstrated in a separate experiment that Δ-$[Co(en)_2(H_2O)(OH)]^{2+}$ racemizes rapidly at pH 6.22 and 25° ($k = 1.75 \times 10^{-3}$ sec^{-1}). Thus kinetic selectivity by a consecutive process is impossible under the preparative conditions.

The reported[4] preference for the Λ-*S* diastereoisomer in the products is also not supported by our experiments. Using both preparative methods[2,4] equal quantities (50 ± 3%) of Λ-*S* and Δ-*S* isomers were isolated following separation on

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(4) J. I. Legg and J. Steele, *Inorg. Chem.*, **10**, 2177 (1971).

cation-exchange resins. Furthermore, mutarotation of the Λ-*S* diastereoisomer to equilibrium in 0.05 *M* NaOH resulted in a similar distribution of the Λ-*S* and Λ-*R* products. Thus in basic solution the free energy difference between the diastereoisomers is close to zero.

Clearly there is no substantial preference either kinetically or thermodynamically for the formation of one isomer relative to the other.

For a summary of results, see Scheme I.

Registry No. $[Co(en)_2CO_3]ClO_4$, 15155-12-1; Λ(+)-$[Co(en)_2$(*S*-glu)$]ClO_4 \cdot H_2O$, 30617-15-3; Δ-$[Co(en)_2$(*S*-glu)$]Cl_2$, 33293-37-7; ΛΔ-$[Co(en)_2$(*S*-glu)$]^{2+}$, 38673-76-6; Δ-(−)D-$[Co(en)_2CO_3]ClO_4 \cdot {}^1/_2H_2O$, 38673-77-7; Δ-(−)D-$[Co(en)_2(OH)(H_2O)]^{2+}$, 38673-78-8; *S*-(+)-glutamic acid, 6899-05-4.

Correspondence

A General Bonding Model for Linear and Bent Transition Metal-Nitrosyl Complexes

Sir:

A recent paper which discussed a qualitative molecular orbital scheme for linear and bent transition metal-nitrosyl complexes[1] prompts me to report some Wolfsberg-Helmholtz calculations for the complex cation $[Co(NO)(NH_3)_5]^{2+}$ [2] (Co-N-O) = 180-90°). These calculations show that the angular distortion of the metal-diatomic ligand moiety from linearity influences the stabilities of only two metal-ligand molecular orbitals substantially. Such a simple result may be readily adapted to other metal-ligand systems and serves as a basis for a very general bonding model.

The calculations were performed using Slater atomic orbitals with exponents suggested by Gouterman.[3] These exponents emulate the overlap integrals of SCF functions for the bond distances of interest. The metal 3d, 4s, and 4p valence-state orbital ionization energies were expressed in a quadratic form to take into account their charge dependence. The necessary parameters were taken from Basch, Viste, and Gray.[4] For the ammine ligands sp^3 hybridization was assumed, and the nitrogen atoms' orbital ionization energies were set equal to the ionization potential of ammonia and the charge dependence suggested by Cotton and Haas[5] was used. Valence-orbital ionization energies suggested by Ballhausen and Gray were used for the nitrosyl nitrogen and oxygen atoms.[6] The off-diagonal elements for the 22 × 22 secular determinant were estimated from $H_{ij} = kS_{ij}(H_{ii} + H_{jj})/2.00$ ($k = 2.25$) and the eigenvalues were calculated to self-consistent charge as judged by a Mulliken population analysis.[7]

Figure 1 shows the energies of the predominantly metal d orbitals and ligand π^* orbitals for the nitrosyl complex with Co-N-O bond angles between 180 and 90° (other orbitals have been omitted from the figure for reasons of clarity). The following points emerge from the calculations.

(a) The $a_1(d_{z^2})$ antibonding metal-ligand σ orbital and the $e_x(\pi^*(NO), d_{xz})$ metal-ligand antibonding orbital have the same symmetry and similar energies in the distorted molecule and consequently mix strongly to give rise to a more bonding, $a'(\pi^*(NO), d_{z^2})$, and less bonding, $a'(d_{z^2}, \pi^*(NO))$, pair of orbitals (for the molecule with Co-N-O ≠ 180° the point group is C_s and all orbitals are either symmetric, a', or antisymmetric, a'', with respect to the plane of symmetry). The energy separation between these orbitals is approximately proportional to the distortion angle (see Figure 1) and electron occupation of the more stable $a'(\pi^*(NO), d_{z^2})$ orbital will lead to an energetically favorable distortion. This behavior is analogous to the stabilization of the $2\pi_x{}^*$ antibonding orbital because of positive overlap with the hydrogen 1s orbital in HNO, when H-N-O ≠ 180°.[8]

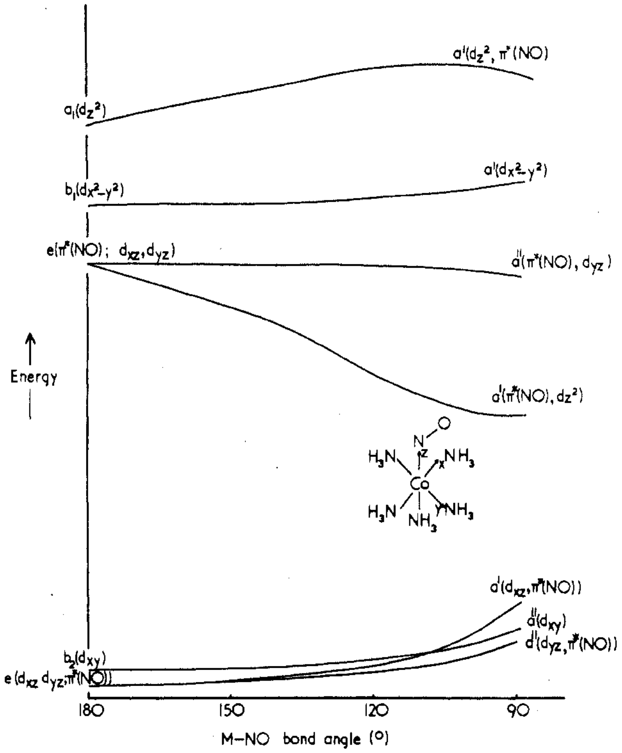

Figure 1. Variation of the molecular orbital energies with Co–N–O bond angle change for $[Co(NO)(NH_3)_5]^{2+}$.

(b) The $e_x(d_{xz}, \pi^*(NO))$ orbital is destabilized to a smaller extent by the distortion because of diminished "π-type" overlap with the ligand π^* orbital.

(c) The energies of the other orbitals shown in the figure and the more stable molecular orbitals not shown in the fig-

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[1] C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, 93, 4905 (1971).

[2] B. A. Coyle, C. S. Pratt, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

[3] M. Zerner and M. Gouterman, *Theor. Chim. Acta*, 4, 44 (1966); *Inorg. Chem.*, 5, 1699 (1966).

[4] H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, 44, 10 (1966).

[5] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 1004 (1964).

[6] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965.

[7] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

[8] (a) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953); (b) B. M. Gimarc, *J. Amer. Chem. Soc.*, 93, 815 (1971).