# The Chemistry of Coordinated Azides

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## Contents

## I. Introduction

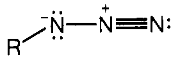
In contrast to the chemistry of organic azides, the chemistry of coordinated azides had received little attention until the early sixties. This was undoubtedly due to the explosive nature of metal azides and their extreme sensitivity to shock. However, when shock resistance and thermal stability became apparent for azido complexes that contain large counterions or a central metal whose oxidation state is stabilized by certain ligands, this area of chemistry gained impetus. Indeed, a considerable amount of information concerning the chemistry of azido complexes is now available particularly owing to the efforts of W. Beck and his coworkers. It is the purpose of this article to review these recent developments in the chemistry of coordinated azides.

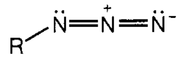
## II. Scope and Limitation

This review, which covers the literature up to the middle of 1972, deals with structural aspects, infrared spectra, and chemical reactivity of coordinated azides. Only those azides that exist as molecular or ionic complexes, as opposed to those containing azide groups which form part of a polymeric network extending throughout the crystal lattice, will be considered. Specifically excluded are material on heavy-metal azides and reactions between metal complexes and organic azides. The former material has been reviewed previously.[1a,b 2a,b]

## III. Structural Aspects of Coordinated Azides

It is well known that the azide ion, $N_3^-$, is linear and symmetric, possessing equal N–N distances which average 1.154 (15) Å[2]. On the other hand, the so-called covalent azides ($HN_3$ or organic azides) are linear[3a] and asymmetric possessing unequal N–N distances.[3b] In this case, the longer bond distance always occurs between the middle nitrogen and the nitrogen which is bonded to the organic moiety. These distances together with the R–$N_3$ angle (the angle between the linear azide group and the R–N bonds) support Pauling's suggestion that the two canonical forms I and II are the main contributors to the ground-state geometry of the $N_3$ group.[4]


I


II

In contrast to the ionic or covalent azides, the equilibrium configuration of coordinated azides is not as predictable. The first structural investigation[5] of an azido complex was carried out in 1964 on the azidopentaamminecobalt(III) complex $[Co(NH_3)_5N_3](N_3)_2$. The coordinated azide was found to be linear and asymmetric with a relatively large Co–$N_3$ angle. Several additional structural reports on azido complexes have appeared since then, and these are listed in Table I together with important structural parameters. It is convenient to divide these complexes into three groups: (a) complexes containing an azide group bound to one metal atom; (b) complexes containing an azide group bridging two metal atoms through the same nitrogen; and (c) complexes containing an azide group bridging two metal atoms through the two end nitrogens. Representative structures for each of these groups are depicted in Figures 1, 2, and 3, respectively.

From examination of those complexes which fall into groups a and b, it is quite apparent that in some cases the azide group is symmetric within experimental error while in others the two N–N distances are significantly different. (We will consider the two distances to be significantly different only if the difference between the two bond lengths is larger than $3\sigma$). It should be noted that in all cases where the azide is asymmetric, the long N–N distance always occurs between the middle nitrogen and the nitrogen which is coordinated to the metal. At the present time, very little can be said about complexes which belong to group c since only one structure of this type has been reported to date.[6] However, we would expect all complexes which belong to this group to contain symmetric azides *(vide infra)*.

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(1) (a) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959); (b) P. Gray, *Quart. Rev., Chem. Soc.*, **17**, 441 (1963).

(2) (a) A. D. Yoffe, "Developments in Inorganic Chemistry," Vol. I, C. B. Colburn, Ed., Elsevier, New York, N. Y.; 1966, p 72. (b) K. G. Mason, "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Suppl II, Part II, Longmans, Green and Co., New York, N. Y., 1967, p 16.

(3) (a) We note one exception: F. W. Felix and M. Müller, *Angew. Chem., Int. Ed. Engl.*, **8**, 915 (1969); (b) See, for example, I. E. Knaggs, *Proc. Roy. Soc., Ser. A*, **150**, 576 (1935); N. Müller, *Z. Anorg. Allg. Chem.*, **382**, 110 (1971).

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1967.

(5) G. H. Palenik, *Acta Crystallogr.*, **17**, 360 (1964).

(6) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971).

**TABLE I. Structural Parameters for Azido Complexes**[a-c]

| | Distances, Å | | | Angles, deg | | |
|---|---|---|---|---|---|---|
| Compound | $M-N_1$ | $N_1-N_2$ | $N_2-N_3$ | $M-N_1-N_2$ | $N_1-N_2-N_3$ | Ref |
| | | Group a | | | | |
| $[Co(NH_3)_5N_3]^{2+}$ | 1.943 (5) | 1.208 (7) | 1.145 (7) | 125.2 (2) | 179.3 (3) | 5 |
| *sym*-$[Co(trenen)N_3]^{2+}$ | 1.957 (6) | 1.209 (7) | 1.152 (7) | 119.0 (5) | 176.4 (9) | 11 |
| *cis*-$[Co(en)_2(N_3)_2]^{+}$ [d] | 1.99 | 1.11 | 1.14 | 120 | 179 | *g* |
| | 1.95 | 1.14 | 1.23 | 119 | 179 | |
| $Ni(P(C_6H_5)_3)_2(NO)N_3$ [e] | 2.018 (8) | 0.977 (9) | 1.282 (11) | 128.1 (9) | 175.1 (11) | *h* |
| $Cu(Et_4dien)BrN_3$ | 1.927 (6) | 1.145 (8) | 1.144 (9) | 125.4 (5) | 175.5 (10) | 16 |
| $Cu_2(diphos)_3(N_3)_2$ | 2.040 (13) | 1.196 (8) | 1.076 (18) | 132.0 (10) | 179.0 (10) | *i* |
| $Zn(C_5H_5N)_2(N_3)_2$ | 1.928 (16) | 1.170 (23) | 1.131 (24) | 128.9 (13) | 173.2 (20) | *j* |
| | 1.945 (17) | 1.153 (27) | 1.133 (26) | 129.0 (13) | 176.3 (19) | |
| $Zn(NH_3)_2(N_3)_2$ | 2.006 (14) | 1.176 (28) | 1.149 (29) | 132.0 (14) | 178.7 (21) | *k* |
| | 1.987 (14) | 1.186 (23) | 1.158 (26) | 129.6 (12) | 176.5 (18) | |
| | 1.963 (42) | | | 124.8 (15) | | |
| $[Fe(N_3)_5]^{2-}$ | 2.041 (15) | 1.16 (3) av | | 125.1 (15) | *n* | *l* |
| | 1.971 (14) | | | (146.0) | | |
| $[Ru(en)_2(N_2)(N_3)]^{+}$ | 2.121 (8) | 1.179 (10) | 1.146 (11) | 116.7 (7) | 180 (1) | *m* |
| | | Group b | | | | |
| | 2.06 (2), 2.07 (2) | 1.24 (3) | 1.16 (3) | | | |
| $[CO_3Mn(N_3)_3Mn(CO)_3]^{-}$ | 2.10 (2), 2.11 (2) | 1.23 (3) | 1.11 (3) | *n* | *n* | 12 |
| | 2.10 (2), 2.05 (2) | 1.20 (3) | 1.20 (3) | | | |
| | 2.004 (13) | 1.239 (14) | 1.142 (13) | 127.8 (13) | 175.1 (14) | |
| $[Pd_2(N_3)_6]^{2-}$ [f] | 2.004 (16) | 1.205 (18) | 1.139 (16) | 120.6 (14) | 173.2 (17) | 10 |
| | | Group c | | | | |
| $[Cu(P(C_6H_5)_3)_2N_3]_2$ | 2.103(7) | 1.184(6) | | 122.3 (8) | 177.8 (8) | 6 |

[a] Values in parentheses are the reported estimated standard deviations. Mean values are given for the last two structures. [b] $N_1$ is the nitrogen atom attached to the metal and $N_2$ is the middle nitrogen atom. [c] Ligand abbreviations are as follows: trenen = (4-(2-aminoethyl)-1,4,7,10-tetraazodecane); en = ethylenediamine; Et₄dien = 1,1,7,7-tetraethyldiethylenetriamine; diphos = 1,2-bis(diphenylphosphino)ethane. [d] Two-dimensional X-ray data only; the reported fractional coordinates are incorrect. [e] It was reported for this structure that the azide group is inadequately described by the model. [f] The first and second lines give mean values for the bridging and terminal azides, respectively. [g] V. M. Padmanabhan, R. Balasubramanian, and K. V. Muralidharan, *Acta Crystallogr. Sect. B*, **24**, 1638 (1968). [h] J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971). [i] A. P. Gaughan, R. F. Ziolo, and Z. Dori, *ibid.*, **10**, 2776 (1971). [j] I. Agrell and N. Vannerberg, *Acta Chem. Scand.*, **25**, 1630 (1971). [k] I. Agrell, *ibid.*, **24**, 1247 (1970). The values given are for one crystallographically independent molecule. [l] J. Drummond and J. S. Wood, *Chem. Commun.*, 1373 (1969). [m] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **9**, 2768 (1970). [n] Values not reported.

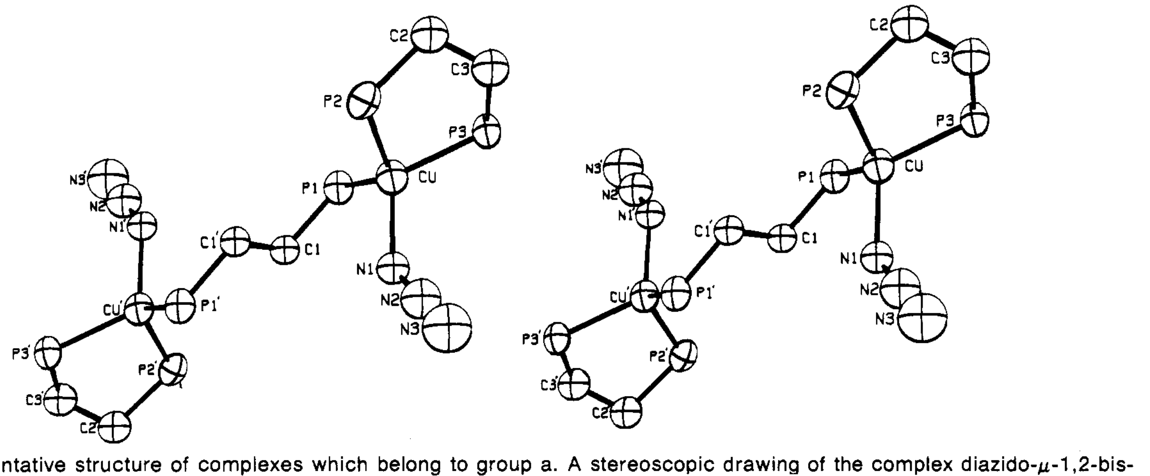

Figure 1. A representative structure of complexes which belong to group a. A stereoscopic drawing of the complex diazido-μ-1,2-bis(diphenylphosphino)ethane)-bis(1,2-bis(diphenylphosphino)ethane)dicopper(I), $Cu_2(diphos)_3(N_3)_2$. The benzene rings are omitted for clarity.

It is appropriate to discuss at this point the nature of the metal-azide bond and the factors which determine the configuration of the azide moiety. Spectroscopic measurements[7,8] on azido complexes of the types $M(N_3)_6^{n-}$ (M = Ru(III), Rh(III), Ir(III), and Pt(IV)) and $M(N_3)_4^{n-}$ (M = Pd(II), Pt(II), and Au(III)) place the azide ligand between diethyl dithiophosphate and sulfur-bonded thiocyanate in the spectrochemical series and between the bromide ion and diethyl dithiophosphate in the nephelauxetic series. From this it can be inferred that for the above complexes the metal-azide bond is largely covalent, and it can be depicted schematically as III.

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(7) H. H. Schmidtke and D. Garthoff, *J. Amer. Chem. Soc.*, **89**, 1317 (1967).

(8) W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schierev, and K. Feldl, *Chem. Ber.*, **100**, 2335 (1967).

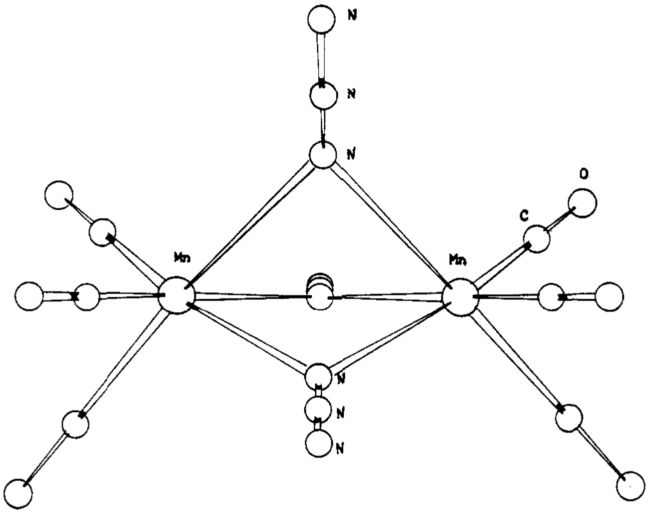


**Figure 2.** A representative structure of complexes which belong to group b. A perspective drawing of the complex $[(CO)Mn(N_3)_3MN(CO_3]^-$.

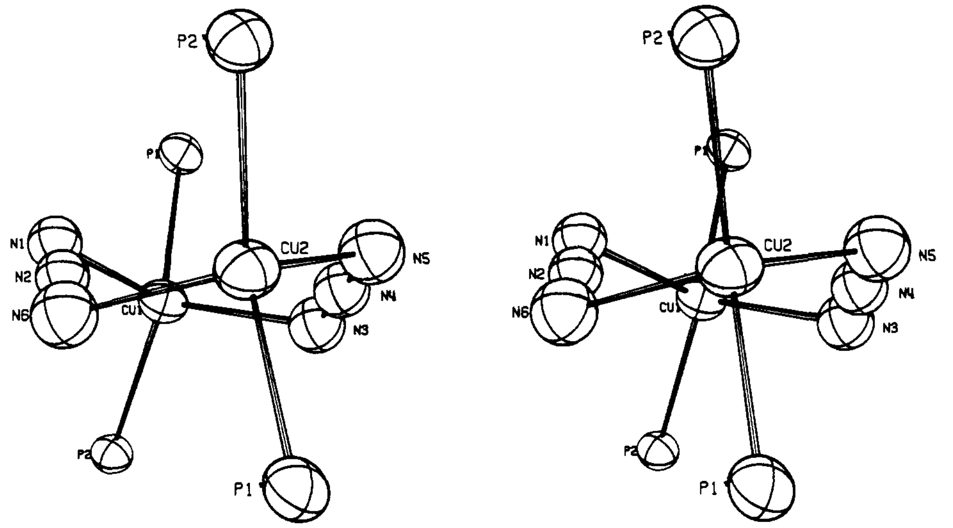
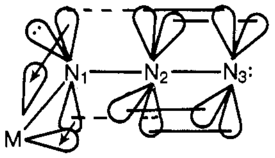
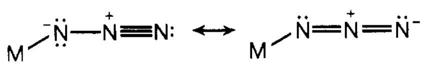


**Figure 3.** A representative structure of complexes which belong to group c. A stereoscopic drawing of the complex $[Cu(P(C_6H_5)_3)_2N_3]_2$. The benzene rings are omitted for clarity.



III

It is reasonable to assume that the larger the $\pi$ interaction between the p orbital on $N_1$ and the d orbitals on the metal, the larger will be the difference between the two N-N distances. On the basis of such an assumption, it can then be suggested that for small such $\pi$ interaction the coordinated azide will be symmetric. However, one cannot overlook the effect of the N-N $\sigma$ bond[9] on the configuration of the azide. Thus, in the complex $Pd_2(N_3)_6^{2-}$ all azides are asymmetric, while the Pd-N distance of 2.004 (8) Å is indicative of single-bond character.[10] It is unfortunate that one cannot assess separately the importance of each of these two kinds of interactions and their relative contribution to the asymmetry of coordinated azides, but it is safe to say that both will depend on the geometry of the complex as a whole, the nature of the other ligands, and the metal atom and its oxidation state. In terms of valence-bond structures we can view the coordination of the azide ligand in a way similar to the one suggested by Pauling for covalent azides, that is, that the two canonical structures shown below are the main contribution to the ground-state geometry of the coordinated azide.



Another structural parameter of interest is the M-$N_3$ bond angle. For group a complexes this angle varies between 117 and 132°, which is within the expected range for the angle of a trigonally hybridized nitrogen. However, this angle may not be very sensitive to electronic factors. For example, within the coordination sphere, all structural parameters of the complexes $[Co(NH_3)N_3]^{2+}$ [5] and $[Co(trenen)N_3]^{2+}$ [11] are almost identical with the exception of the Co-$N_3$ angle which differs by 6°. Thus it appears that steric factors and/or crystal packing also influence the value of this angle.

The coordination mode of the azide group, in contrast to its configuration, is easily predicted, and in all azido complexes only the end-on coordination mode is known. The azide group, however, may be monocoordinated or bridging with the degree of coordination depending on the requirements of the complex as a whole. In binuclear

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(9) R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **10**, 38 (1971).

(10) W. P. Fehlhammer and L. D. Dahl, *J. Amer. Chem. Soc.*, **94**, 3377 (1972).

(11) I. E. Maxwell, *Inorg. Chem.*, **10**, 1782 (1971).

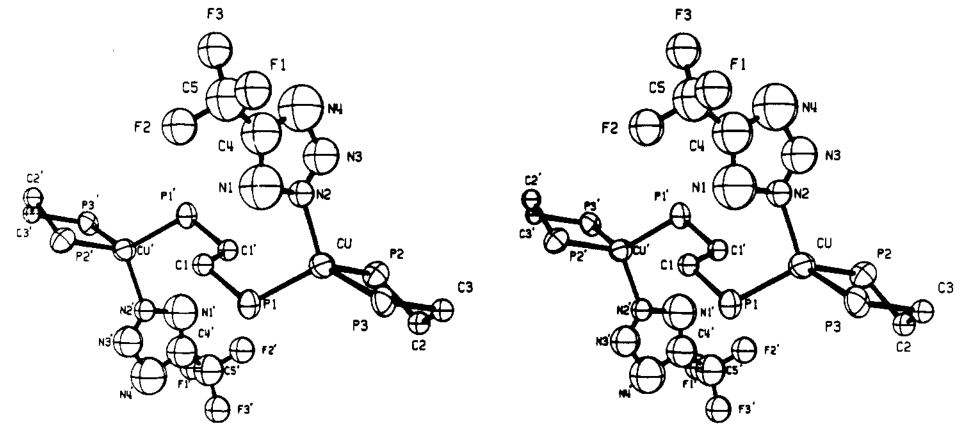
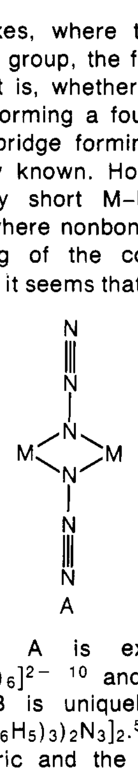
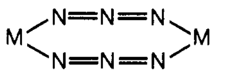


**Figure 4.** A stereoscopic drawing of the $CF_3CN$ adduct of the complex $Cu_2(diphos)_3(N_3)_2$.

complexes, where the azide group may function as a bridging group, the factors influencing the mode of bridging, that is, whether the azide coordinates as a one-end bridge forming a four-membered ring (A) or as an end-to-end bridge forming an eight-membered ring (B), are not fully known. However, a structure of type A with a relatively short M-M distance will be unfavorable in cases where nonbonded repulsions will increase owing to crowding of the coordination sphere. Thus on steric grounds it seems that a structure of type B is preferable.[11a]


A


B

Mode A is exemplified in the structures of $[Pd_2(N_3)_6]^{2-}$ [10] and $[(CO)_3M_n(N_3)_3M_n(CO)_3]^-$,[12] while mode B is uniquely exemplified in the structure of $[Cu(P(C_6H_5)_3)_2N_3]_2$.[5] In the latter compound the azide is symmetric and the eight-membered heteroatom ring is distinctly nonplanar as is evident from Figure 4. The two azide groups are tilted at an angle of 38.8 (5)° with respect to one another, and each $Cu-N_3-Cu$ bridge is significantly nonplanar. Two factors which may contribute to this unusual geometry are, first, packing effects which optimize the efficiency of the packing and minimize the nonbonded repulsions between the phenyl rings of the triphenylphosphine groups and, second, the allenic nature of the middle nitrogen which together with the trigonal hybridization of the terminal nitrogens oppose the planarity of the $Cu-N_3-Cu$ bridge.

## *IV. Infrared Spectra of Coordinated Azides*

The coordination of azides to transition metals can easily be detected by an intense infrared absorption band which occurs above 2000 $cm^{-1}$. (For a comprehensive listing of infrared data, see ref 8.) This band is associated with the azide antisymmetric stretch, $\nu_{as}(N_3)$, and its energy depends, to a first approximation, only on the configuration of the bonded azide, that is, on the degree of its symmetry. Thus, the larger the difference between the two N-N distances ($\Delta d$), the higher is the energy of $\nu_{as}(N_3)$. For example, in $Cu(N_3)_2$,[13] $\Delta d$ for one of the structurally independent azides is 0.12 Å for which $\nu_{as}(N_3)$ occurs at 2128 $cm^{-1}$, while in $Cu(N_3)_2(NH_3)_2$,[14] where $\Delta d$ is 0.05 Å for one of the structurally independent azides, $\nu_{as}(N_3)$ occurs at 2080 $cm^{-1}$. Furthermore, a plot of $\nu_{as}(N_3)$ *vs.* $\Delta d$ appears[15] to indicate that there is a simple linear relationship between the degree of the asymmetry of the coordinated azide and the energy of the antisymmetric stretch.

Generalizations such as the above, however, should always be viewed with caution. In the complex $[Pd_2(N_3)_6]^{-2}$,[10] $\nu_{as}(N_3)$ for one of the terminal azides ($\Delta d$ = 0.09 Å) occurs at 2033 $cm^{-1}$, while in the complex $Cu(Et_4dien)Br(N_3)$,[16] where the azide is symmetric, $\nu_{as}(N_3)$ occurs at 2053 $cm^{-1}$. Thus it appears that such generalizations are valid only if one deals with a series of related or similar complexes.

The azide symmetric stretch, $\nu_{sy}(N_3)$, occurs at about 1300 $cm^{-1}$, and, although weak, it has been observed in many of the azido complexes studied to date.[8] Both the intensity and the energy of $\nu_{sy}(N_3)$ depend to a large extent on the degree of asymmetry of the coordinated azide, and, as was the case with $\nu_{as}(N_3)$, there appears to be a simple relationship[15] between $\Delta d$ and $\nu_{sy}(N_3)$. In this case, the larger the value of $\Delta d$, the lower the energy of $\nu_{sy}(N_3)$. However, the same caution should be exercised for correlations of $\nu_{sy}(N_3)$ as was suggested in the previous paragraph for $\nu_{as}(N_3)$. Furthermore, Raman data, which have been lacking particularly for coordinated azides, would aid in making future assignments.

The doubly degenerate bending vibration $\nu_b$, occuring between 500 and 700 $cm^{-1}$ for the azide group, has been reported for several azide complexes[8] but appears to be of less diagnostic value than either of the stretching vibrations.

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(11a) Note Added in Proof. Two metal atoms, bridged by a single azide ligand, have recently been described: K. V. Werner and W. Beck, *Chem. Ber.*, **105**, 3209 (1972).

(12) R. Mason, G. A. Rusholme, W. Beck, H. Engelmann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Commun.*, 496 (1971).

(13) I. Agrell, *Acta Chem. Scand.*, **21**, 2647 (1967); R. Söderquist, *Acta Crystallogr.*, **B24**, 450 (1968).

(14) I. Agrell, *Acta Chem. Scand.*, **20**, 1281 (1966).

(15) I. Agrell, *ibid.*, **25**, 2965 (1971).

(16) R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, submitted for publication.

In summary it can be said that the stretching vibrations offer a quick and reliable identification in cases where the presence of coordinated azide is suspected. The stretching vibrations are not, however, as reliable for identifying the equilibrium configuration of the azide and one should avoid making comparisons between markedly different complexes, that is, between complexes which are of different geometry or which contain different metal atoms in different oxidation states. Moreover, in most cases, the degree of coordination of the azide ligand, that is, whether it is monocoordinate or bridging, cannot be established solely from a consideration of infrared data.[16] One exception to this limitation is the case of binuclear complexes where both bridging and terminal azides are suspected. In this case the suspicion may be confirmed by the observation of two asymmetric stretching frequencies with the higher frequency stretch generally assigned to the bridging group. We note, however, that the mode of the bridge in these and other binuclear complexes, that is, modes A or B as depicted above, cannot be ascertained from the number of infrared active vibrations since both structures have $D_{2h}$ symmetry.

## *V. The Chemistry of Coordinated Azides*

### A. Oxidation of Coordinated Azides

It is well known that azide ions react with $HNO_2$[17] to yield a nitrosyl azide intermediate which readily decomposes to yield $N_2$ and $N_2O$ as shown in eq 1. This reaction was used by Haim and Taube[18] to produce the first example of a reaction of a coordinated azide. Thus, in the absence of coordinating anions, the complex $[Co(NH_3)_5N_3]^{2+}$ reacts with $HNO_2$ in aqueous solution according to eq 2.

$$N_3^- + HNO_2 + H^+ \longrightarrow [H_2O + N_3NO] \longrightarrow N_2 + N_2O + H_2O \quad (1)$$

$$[Co(NH_3)_5N_3]^{2+} + HNO_2 + H^+ \longrightarrow [Co(NH_3)_5OH_2]^{3+} + N_2 + N_2O \quad (2)$$

In the presence of coordinating anions X (X = $Cl^-$, $Br^-$, $NO_3^-$, $NCS^-$), the complexes $[Co(NH_3)_5X]^{2+}$ are formed in addition to the aquo complex. It was suggested that the reaction proceeds by way of the intermediate $[Co(NH_3)_5N_3NO]^{3+}$ which loses $N_2$ and $N_2O$ to form the pentacoordinated intermediate $[Co(NH_3)_5]^{3+}$. This reaction, which leaves a vacant coordination site, had recently been used by Beck, *et al.*, to synthesize azide-bridged complexes of Pd(II) and Pt(II)[19] as depicted in eq 3.

$$2[(Ph_3P)_2M(N_3)_2] + 2NO^+X^- \xrightarrow[CH_2Cl_2]{20^\circ} [(Ph_3P)_4M_2(N_3)_2]^{2+} + 2X^- + 2N_2 + 2N_2O \quad (3)$$

$$X = BF_4^-, ClO_4^-, PF_6^-$$

M = Pd(II), Pt(II); $Ph_3P$ = triphenylphosphine

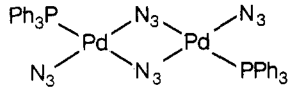
The bridging mode of the azide has been suggested to be that of type A *(vide supra)*. Similarly, the dimer can be obtained by reaction with other Lewis acids such as $BF_3$.[20] The oxidation of coordinated azide can be accomplished also by $N_2O_3$ as shown below.[20]

$$(Ph_3P)_2Pd(N_3)_2 + 2N_2O_3 \longrightarrow (Ph_3P)_2Pd(NO_2)_2 + 2N_2 + 2N_2O \quad (4)$$

Similarly, the reaction of $(Ph_3P)_2Pd(N_3)_2$ with nitrogen dioxide leads to the formation of a palladium nitrato complex.[21] Treatment of this palladium complex with nitric acid (eq 5) leads to the oxidation of triphenylphosphine

$$2[(Ph_3P)_2Pd(N_3)_2] + 4NO \longrightarrow [(Ph_3P)_2Pd_2(N_3)_4] + 2Ph_3PO + 2N_2O \quad (5)$$

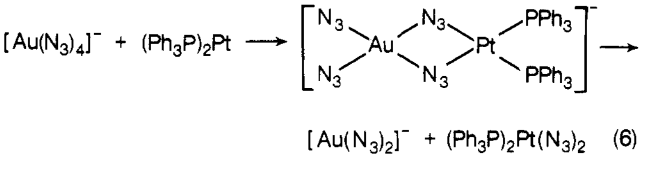
and the formation of an azide-bridged dimer whose structure is believed to be IV.



IV

Feltham[22] has reported some interesting reactions of the complex $RuN_3Cl(das)_2$ (das = *o*-phenylenebis(dimethylarsine)) with $O_2$ and $NOPF_6$. In the presence of light, the azide is oxidized by dioxygen to give $[RuCl(NO_2)(das)_2]$, while $NOPF_6$ converts the coordinated azide to a coordinated dinitrogen. This last reaction was also mentioned[23] as a useful route for the preparation of *cis*-$[Ru(en)_2(N_2)_2]^{2+}$ from *cis*-$[Ru(en)_2N_2N_3]^+$.

Another interesting reaction which can be considered here is the reaction between $Au(N_3)_4^-$ and $(Ph_3P)_nPt$ ($n$ = 3, 4) in THF-benzene solution.[24] This reaction, which leads to the formation of $(Ph_3P)_2Pt(N_3)_2$, can be viewed as an oxidative addition of $N_3$ radicals to the Pt(0) complex, and it is reasonable to suggest that the reaction proceeds by a bridged mechanism as depicted in eq 6. This mechanism was previously suggested for the electron-transfer reaction between $Cr^{2+}$ and $Cr(N_3)_2^+$.[25]



(6)

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[17] G. Stedman, *J. Chem. Soc.*, 1702 (1960).

[18] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

[19] W. Beck, P. Kreutzer, and K. v. Werner, *Chem. Ber.*, **104**, 528 (1971).

[20] W. P. Fehlhammer, W. Beck, and P. Pöllmann, *Chem. Ber.*, **102**, 3093 (1969).

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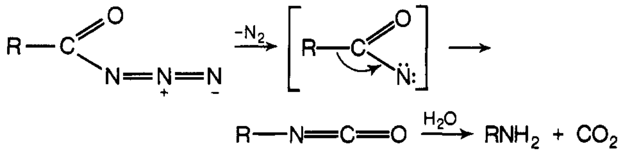
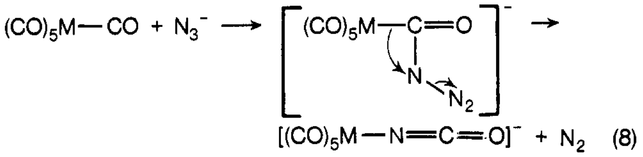
## B. Reactions Involving Cleavage of the MN–N$_2$ Bond

A well-established method, known as the Curtius rearrangement,[26] for the preparation of primary amines, involves the loss of nitrogen from an acyl azide to form an acyl nitrene. The latter rearranges to the isocyanate, which upon hydrolysis gives the amine and carbon dioxide



An analogous reaction is also observed for the reaction of azide ions with metal carbonyls. For example, W(CO)$_6$ reacts with azide ion[27] according to eq 7. This reaction is believed to proceed by an attack of the azide ion on the somewhat electrophilic carbon atom[28] followed by rearrangement and loss of N$_2$ to form the coordinated isocyanate as depicted in eq 8.

$$W(CO)_6 + N_3^- \longrightarrow [W(CO)_6NCO]^- + N_2 \qquad (7)$$



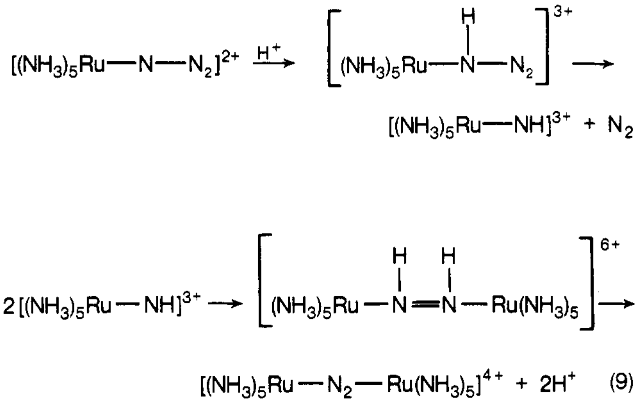
(8)

M = Cr, Mo, W

A similar reaction also occurs with cationic carbonyl complexes such as $C_5H_5Fe(CO)_3^+$.[29] The formation of coordinated isocyanate can also be achieved by the reaction of carbon monoxide with a variety of azido complexes[30] such as $(Ph_3P)_2M(N_3)_2$ (M = Pd(II), Pt(II)), $(Ph_3P)_3RhN_3$, $(Ph_3P)_2Ir(CO)N_3$, and $[Au(N_3)_2]^-$. On the basis of kinetic data,[31] it has been suggested that the first step in this reaction is the binding of CO to the metal followed by a rearrangement similar to the one depicted above.

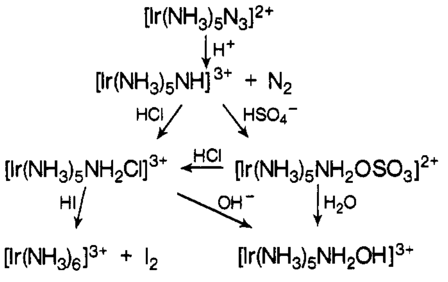
Coordinated thiocyanates too can be obtained by an analogous method. For example, the complex $[C_5H_5Fe(CO)_2CS]^-$ reacts with azide ions[32] to give $[C_5H_5Fe(CO)_2NCS]$ and N$_2$, while $(Ph_3P)_2Ir(CO)NCS$ can be prepared from the reaction of the corresponding azide complex with a thiocarbonyl under mild pressure.[33]

The reactions discussed above are of particular interest since they involve the heterolytic cleavage of the MN–N$_2$ bond which is a prerequisite for the formation of the long-sought coordinated nitrene intermediate. Stabilization of the electron-deficient nitrene by coordination to transition metals has been hypothesized,[34] and recently the copper-catalyzed decomposition of benzenesulfonylazide has been proposed to involve a copper–nitrene intermediate.[35] However, the first well-established example of a metal–nitrene[36] comes from the acid-catalyzed decomposition of $[Ru(NH_3)_5N_3]^{2+}$ which leads to the formation of the dinitrogen-bridged complex $[(NH_3)_5Ru\text{-}N_2\text{-}Ru(NH_3)_5]^{4+}$. This reaction is thought to proceed as depicted in eq 9. In support for this mechanism, it was noted that the formation of the dinitrogen dimer is quenched when the reaction is carried out in the presence of small amounts of thiourea, diethyl sulfide, or iodide. Also, the yield of the dimer decreases with increasing initial concentration of $[Ru(NH_3)_5N_3]^{2+}$ which suggests that this complex by itself can function as a trap for the coordinated nitrene intermediate. In addition, the successful isolation[37] of $[(NH_3)_5CoNHN_2]^{3+}$ lends strong support for the protonation of the coordinated azide as the first step in this reaction.



More direct evidence for the formation of a coordinated nitrene intermediate[38] comes from the reactions of $[Ir(NH_3)_5N_3]^{2+}$ in acidic solution. These reactions, which are summarized in Scheme I, clearly demonstrate the electrophilic nature of the electron-deficient nitrogen which also characterizes the chemistry of singlet organic nitrene.[39]

**SCHEME I**



The reactions of $[Ir(NH_3)_5N_3]^{2+}$ differ from those observed for the ruthenium complex discussed above in that the formation of the bridged dinitrogen complex[36] is accompanied by reduction of Ru(III) to Ru(II), a pathway not available for the Ir(III) complex.

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The electron-deficient nitrogen in $[Ir(NH_3)_5NH]^{3+}$ is undoubtedly stabilized by $d\pi \rightarrow p\pi$ interaction which is believed to be responsible for the unusual stability of aminonitrene.[40] In those cases where the metal has two easily accessible oxidation states which differ by two electrons, such as Re(III) and Re(V), the $d\pi \rightarrow p\pi$ interaction can lead to the transfer of an electron pair to the electron-deficient nitrogen, resulting in a complex which is best formulated as metal nitride.[41] Thus, the complex $\{Re[P(C_6H_5)(CH_3)_2]_3Cl_3\}$ reacts very readily with $N_3^-$ to give $\{Re[P(C_6H_5)(CH_3)_2]_3Cl_2N\}$ and $N_2$. The intermediate azido complex cannot be isolated,[42] and it is reasonable to suggest that the heterolytic cleavage of the coordinated azide is facilitated by the two-electron oxidation of the metal as depicted below.[41] This formulation is supported

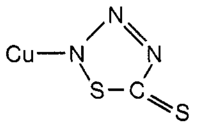
$$L_5Re^{III}—N—N_2 \longrightarrow L_5Re^{V}\equiv N + N_2$$

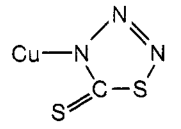
by the fact that the coordinated nitrogen atom is stable toward nucleophiles and by the short Re–N distance[43] (1.602 (9) Å) which clearly indicates a multiple bond. As a further support for this formulation, we note that the formation of $[MoCl_4N]^-$ [44] from $MoCl_5$ and $N_3^-$ is accompanied by liberation of $Cl_2$ in addition to $N_2$, while its formation from $MoCl_4$ and $N_3^-$ is accompanied only by the liberation of $N_2$.

## C. 1,3-Dipolar Cycloaddition Reactions

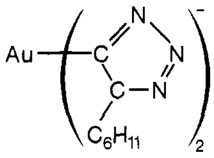
Organic azides are known to react with olefins by 1,3-dipolar cycloaddition to form heterocyclic compounds which may decompose thermally or photolytically to yield a variety of products.[45] By analogy with organic azides, azido complexes of transition metals might be expected in some cases to undergo the same type of reactions, and, indeed, this has been borne out in a number of cases.

The addition of $CS_2$ to a chloroform solution of $Cu(P(C_6H_5)_3)_2N_3$[46] results in a clear yellow solution which upon photolysis evolves nitrogen, deposits colloidal sulfur, and leaves a colorless solution from which $Cu(P(C_6H_5)_3)_2NCS$ can be isolated. The formation of the yellow compound can be followed by the disappearance of the azide asymmetric stretch and the appearance of a sharp band at 1235 $cm^{-1}$ which can be associated with a thiocarbonyl group. It is therefore reasonable to suggest that the addition occurs at the azide moiety, possibly by a 1,3-dipolar cycloaddition. Possible structures for the addition product are V and VI. The dipolarophile carbon disulfide reacts with a variety of other azido complexes,[47] and in all cases the resulting thiothiatriazole ring decomposes thermally and or photolytically to give the corresponding thiocyanate complexes.


V


VI

Another dipolarophile which readily reacts with several azido complexes is trifluoroacetonitrile. Formation of the stable heterocyclic ring, perfluoromethyltetrazole,[47,48] upon addition of trifluoroacetonitrile to the azide moiety, has been unequivocally established by X-ray diffraction techniques in two cases.[49,50] One such structure is shown in Figure 4. This complex was obtained from the addition of $CF_3CN$ to diazido-$\mu$-1,2-bis(diphenylphosphino)ethane - bis(1,2 - bis(diphenylphosphino)ethane)dicopper(I), $Cu_2((CH_2P(C_6H_5)_2)_2)_3(N_3)_2$. In addition, Beck has reported that several isonitriles[51] also react in a similar manner, and in some cases the resulting tetrazole ring is bound to the metal through the ring carbon atom. Thus, cyclohexyl isocyanide reacts with $Au(N_3)_2^-$ to give the complex VII.


VII

## D. The Photochemistry of Coordinated Azides

The first studies on the photochemistry of coordinated azides were reported in the early fifties by Linhard and coworkers[52] who examined the photolysis of the complex $[Co(NH_3)_5N_3]^{3+}$. It was suggested then, and later confirmed by Endicott,[53] that the stoichiometry of this reaction can best be described by eq 10. Thus, irradiation of the complex at 2537 Å leads to oxidation–reduction photodecomposition with the generation of azide radicals which collapse to give molecular nitrogen. The observation that $I^-$, a scavenger for $N_3\cdot$, can nearly completely quench the $N_2$ yield is strong evidence for the production of azide radicals in this photoreaction. Flash photolysis experiments also indicate that this is indeed the case.[54] It is interesting to note that irradiation at 3700 Å also leads to the production of $N_3\cdot$.

$$[Co(NH_3)_5N_3]^{2+} + h\nu + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + 1.5N_2 \quad (10)$$

Similar behavior is observed in the photolysis of an aqueous solution of azidopentaamminechromium(III)[55] when the irradiation is carried out in the charge-transfer region, *i.e.*, 2630 and 3130 Å. When the irradiation is restricted to the region of ligand field bands, only

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$[Cr(NH_3)_4(H_2O)N_3]^{2+}$ is formed and the release of $N_3^-$ is negligible. In fact, there are no clear examples for substitution reactions involving the release of azide ions upon irradiation of ligand field bands.

Several other examples of the oxidation-reduction photodecomposition of azido complexes are also known. An interesting reaction is the photochemical decomposition[56] of $[Pt(dien)N_3]^+$ (dien = diethylenetriamine) upon irradiation at 2540 or 3130 Å (these are apparently L → M charge-transfer transitions). The photolysis leads to the formation of azide radicals in the primary photochemical process which in turn necessitates the initial formation of the unstable complex $[Pt(dien)]^+$. As previously mentioned, reactions of this type have been thought to occur only when the metal atom has a relatively stable one-electron reduction product. Finally, we might add that the photoredox reactions described above have found commercial use in the photoinitiation of radical polymerization.[57]

From the photochemical data available to date, it is quite clear then that the photochemistry of coordinated azides is governed by the homolytic cleavage of the metal-nitrogen bond. In contrast, organic azides are known to decompose photolytically or thermally by the heterolytic cleavage of the $N-N_2$ bond to give a nitrene and molecular nitrogen.[58]

Although some indication for the photochemical cleavage of the $MN-N_2$ bond has been obtained from the photolysis of $Cu(P(C_6H_5)_3)_2N_3$ in $CHCl_3$,[59] an authentic and clear-cut example for the photochemical generation of coordinated nitrene from an azido complex has only recently been reported by Reed, *et al.*[60] Thus, the complex $[Ir(NH_3)_5N_3]^{2+}$ decomposes photolytically to give the intermediate $[Ir(NH_3)_5NH]^{3+}$ which undergoes the same reactions as previously described for the acid decomposition of the same parent compound.[38]

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