triazole)copper(II) ($J/k = -17.9$ to -19.0°K) than in copper(II) benzoate trihydrate ($J/k = -12.7$°K), despite the fact that the Cu–Cu distance of 3.40 Å in the former is longer than 3.15 Å in the latter. Therefore, the superexchange interaction rather than the interaction of direct nature is predominant. This conclusion is supported by the existence of spin densities in the ligand atoms of dichloro(1,2,4-triazole)copper(II).[15] Thus, although normal magnetic moments have been observed for these compounds at room temperature, the spins are not free from one another, but antiferromagnetic interaction exists between neighboring spins in a chain.

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Contribution from Istituto di Chimica Generale
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The Nitrogen–Nitrogen Stretching Band in Hydrazine Derivatives and Complexes

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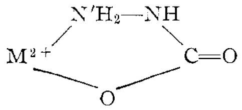
The repulsion between the lone electron pairs of the nitrogen atoms in the staggered hydrazine molecule influences the length of the nitrogen–nitrogen bond; diminution of the repulsion causes shortening of the bond in those derivatives of hydrazine where the lone pair is attracted to bonds. The infrared spectra of several hydrazine derivatives have been examined: the shifts of ν(N–N) are in agreement with this point of view. The band shifts from 880 toward 1000 cm^{-1} when the repulsion between the lone pairs diminishes. In metal complexes of hydrazine, shifts of the band are also observed, depending on the field effect of the metal cations on the lone pairs, even if the nitrogen–nitrogen bond distance remains unaltered.

The hydrazine molecule $H_2N–NH_2$ is composed of two tetrahedra in staggered configuration,[1,2] one corner in each being occupied by a lone pair. The nitrogen–nitrogen bond distance is N–N = 1.46 Å[3] in solid hydrazine but it becomes shorter in the cation $^+H_3N–NH_3^+$ (N–N = 1.40 Å[4]) and in the cation $H_2N–NH_3^+$ (N–N = 1.432,[5] 1.435 Å[6]). This shortening cannot be attributed to increments in π bonding as for diformylhydrazine[7] but more likely to diminution or suppression of the repulsion between the lone pairs.[8] Also in chelates of hydrazinecarboxylic acid, $H_2N'NHCOOH$, the bond between nitrogen atoms is shorter (N–N = 1.43,[6] 1.39,[9] 1.40,[10] 1.43, 1.37,[11] 1.41[12] Å) than in the hydrazine molecule, and again double bonding cannot be invoked to explain the contraction of the bond. As a matter of fact, in the chelate rings



the atoms NH–COO lie in one plane and form a conjugate system, but N′ is out of this plane and does not take part in the conjugation. In these compounds, conjugation of one lone pair with the carboxylato group, accompanied by change of configuration of the nitrogen atom from sp^3 to sp^2, diminishes the repulsion between lone pairs. On the contrary no such shortening of N–N is observed when the hydrazine molecule behaves as a ligand, either bridging (N–N = 1.46 Å[2,13–15]) or unidentate (N–N = 1.46 Å[9]).

The infrared spectra of a large number of hydrazine compounds or derivatives have now been examined in order to confirm these views.

The following sets of compounds have been prepared and examined: (i) compounds containing unidentate N_2H_4 ligands, (ii) compounds containing N_2H_4 bridging groups, (iii) compounds of hydrazinium cations, $H_2N–NH_3^+$, and (iv) compounds of hydrazinecarboxylic acid and of hydrazinedithiocarboxylic acid.

Experimental Section

Preparation.—(i) The compounds bis(hydrazine)bis(hydrazinecarboxylato-N′,O)metal(II), $(N_2H_4)_2(H_2N'–NH–COO)_2M^{II}$, with M^{II} = Co, Ni, or Zn, were prepared from aqueous solutions of salts of the metal, hydrazine hydrate, and carbon dioxide.[16] *Anal.* Calcd for $Co(N_2H_4)_2(H_2N'–NH–COO)_2$: N, 41.03; Co, 21.58. Found: N, 40.90; Co, 21.63. Calcd for $Ni(N_2H_4)_2(H_2N'–NH–COO)_2$: C, 8.80; H, 5.17; N, 41.06; Ni, 21.51. Found: C, 8.90; H, 5.63; N, 41.00; Ni, 21.35. Calcd for $Zn(N_2H_4)_2(H_2N'–NH–COO)_2$: C, 8.59; H, 5.05; N, 40.08; Zn, 23.39. Found: C, 8.81; H, 5.13; N, 39.92; Zn, 23.20.

(ii) (a) The compounds $[M^{II}(N_2H_4)_2]_nX_{2n}$, with M^{II} = Mn, Fe, Co, Ni, Zn, Cd and X = Cl, Br, I, NCS, CH_3COO, were prepared by mixing ammonia, hydrazine hydrate, and salts of

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the metal[17,18] in aqueous solution. *Anal.* Calcd for $[Mn(N_2H_4)_2]Cl_2$: N, 29.50; Cl, 37.33; Mn, 28.93. Found: N, 29.64; Cl, 37.09; Mn, 28.98.

The remaining compounds of this isostructural set were identified unequivocally by powder photographs. *Anal.* Calcd for $[Mn(N_2H_4)_2]Br_2$: Br, 57.32. Found: Br, 57.20. Calcd for $[Zn(N_2H_4)_2]Br_2$: Br, 55.25; N_2H_4, 22.16; Zn, 22.60. Found: Br, 54.92; N_2H_4, 22.12; Zn, 22.52. Calcd for $[Cd(N_2H_4)_2]Br_2$: Br, 47.52; N_2H_4, 19.06; Cd, 33.42. Found: Br, 47.38; N_2H_4, 19.07; Cd, 33.34. Calcd for $[Mn(N_2H_4)_2]I_2$: I, 68.07; N_2H_4, 17.19. Found: I, 67.54; N_2H_4, 16.88. Calcd for $[Zn(N_2H_4)_2]I_2$: I, 66.22; N_2H_4, 16.72; Zn, 17.06. Found: I, 65.98; N_2H_4, 16.57; Zn, 17.26. Calcd for $[Cd(N_2H_4)_2]I_2$: I, 58.98; N_2H_4, 14.89; Cd, 26.12. Found: I, 58.54; N_2H_4, 15.28; Cd, 26.16. Calcd for $[Mn(N_2H_4)_2](NCS)_2$: N, 35.74; NCS, 49.39; Mn, 23.36. Found: N, 35.44; NCS, 49.30; Mn, 23.42. Calcd for $[Fe(N_2H_4)_2](NCS)_2$: N, 35.60; NCS, 49.20; Fe, 23.65. Found: N, 35.93; NCS, 49.00; Fe, 23.37. Calcd for $[Co(N_2H_4)_2](NCS)_2$: N, 35.14; NCS, 48.56; Co, 24.64. Found: N, 34.89; NCS, 48.45; Co, 24.70. Calcd for $[Ni(N_2H_4)_2](NCS)_2$: N, 35.18; Ni, 24.52. Found: N, 35.52; Ni, 24.51. Calcd for $[Zn(N_2H_4)_2](NCS)_2$: N, 34.22; NCS, 47.28; Zn, 26.62. Found: N, 34.12; NCS, 47.23; Zn, 26.58. Calcd for $[Cd(N_2H_4)_2](NCS)_2$: N, 28.72; NCS, 39.69; Cd, 38.41. Found: N, 28.95; NCS, 39.22; Cd, 38.46. Calcd for $[Mn(N_2H_4)_2](CH_3COO)_2$: N, 23.63; Mn, 23.17. Found: N, 23.54; Mn, 23.24. Calcd for $[Zn(N_2H_4)_2](CH_3COO)_2$: N, 26.41; Zn, 22.63. Found: N, 26.20; Zn, 22.72. Calcd for $[Cd(N_2H_4)_2](CH_3COO)_2$: N, 19.02; Cd, 38.16. Found: N, 18.69; Cd, 38.14.

(b) The compounds $[M^{II}(N_2H_4)_3](NO_3)_2$, with M^{II} = Mn, Co, Ni, Zn, or Cd, were prepared by mixing ammonia, hydrazine hydrate, and nitrates of the metals in aqueous solution.[19] *Anal.* Calcd for $[Mn(N_2H_4)_3](NO_3)_2$: N, 40.74; Mn, 19.97. Found: N, 40.26; Mn, 19.82. Calcd for $[Co(N_2H_4)_3](NO_3)_2$: N, 40.15; Co, 21.12. Found: N, 39.98; Co, 21.22. Calcd for $[Ni(N_2H_4)_3](NO_3)_2$: N, 40.19; Ni, 21.05. Found: N, 40.15; Ni, 21.00. Calcd for $[Zn(N_2H_4)_3](NO_3)_2$: N, 39.24; Zn, 22.90. Found: N, 39.35; Zn, 22.87. Calcd for $[Cd(N_2H_4)_3](NO_3)_2$: N, 33.70; Cd, 33.80. Found: N, 33.86; Cd, 33.40.

(iii) (a) The compounds hydrazinium tris(hydrazinecarboxylato-N′,O)metalate(II) monohydrate, $(N_2H_5)[M^{II}(H_2N'{-}NH{-}COO)_3]\cdot H_2O$, with M^{II} = Fe, Co, Ni, or Zn, were prepared from aqueous solutions of the metal salt and hydrazine hydrate, saturated with CO_2.[20] *Anal.* Calcd for $(N_2H_5)[Fe(H_2N'{-}NH{-}COO)_3]\cdot H_2O$: N, 33.75; Fe, 16.82. Found: N, 33.88; Fe, 16.61. Calcd for $(N_2H_5)[Co(H_2N'{-}NH{-}COO)_3]\cdot H_2O$: C, 10.75; H, 4.81; N, 33.44; Co, 17.59. Found: C, 10.59; H, 4.64; N, 33.58; Co, 17.57. Calcd for $(N_2H_5)[Ni(H_2N'{-}NH{-}COO)_3]\cdot H_2O$: C, 10.76; H, 4.82; N, 33.46; Ni, 17.53. Found: C, 11.00; H, 4.99; N, 34.08; Ni, 17.53. Calcd for $(N_2H_5)[Zn(H_2N'{-}NH{-}COO)_3]\cdot H_2O$: C, 10.55; H, 4.72; N, 32.81; Zn, 19.14. Found: C, 10.29; H, 5.05; N, 32.97; Zn, 19.60.

(b) The compounds dihydrazinium tetrachlorocadmiate, $(N_2H_5)_2CdCl_4$, and trihydrazinium pentachlorocadmiate, $(N_2H_5)_3CdCl_5$, were prepared by evaporating, at room temperature, aqueous solutions of hydrazinium chloride and cadmium chloride.[21] *Anal.* Calcd for $(N_2H_5)_2CdCl_4$: Cl, 44.27; N_2H_4, 20.01; Cd, 35.09. Found: Cl, 44.37; N_2H_4, 19.56; Cd, 34.87. Calcd for $(N_2H_5)_3CdCl_5$: Cl, 45.59; N_2H_4, 24.72; Cd, 28.81. Found: Cl, 45.74; N_2H_4, 24.28; Cd, 28.65.

(c) The hydrazinium hydrazinedithiocarboxylate, $(N_2H_5)(H_2N'{-}NH{-}CSS)$, was prepared from hydrazine hydrate and carbon disulfide,[22] mp 124°. *Anal.* Calcd for $(N_2H_5)(H_2N'{-}NH{-}CSS)$: N, 39.94. Found: N, 40.05.

(iv) (a) The hydrazinecarboxylic acid, $H_2N'{-}NH{-}COOH$, was obtained from hydrazine hydrate and carbon dioxide.[23] *Anal.* Calcd for $H_2N'{-}NH{-}COOH$: C, 15.79; H, 5.30; N, 36.83. Found: C, 15.00; H, 5.33; N, 37.50.

(b) The compounds of the isomorphous set, potassium tris(hydrazinecarboxylato-N′,O)metalate(II), $K[M^{II}(H_2N'{-}NH{-}COO)_3]$, with M^{II} = Fe, Co, Ni, or Zn, were obtained from the mother liquors of the compounds $(N_2H_5)[M^{II}(H_2N'{-}NH{-}COO)_3]\cdot H_2O$, treated by potassium hydrogen carbonate.[24,25] *Anal.* Calcd for $K[Fe(H_2N'{-}NH{-}COO)_3]$: C, 11.26; N, 26.26; K, 12.22; Fe, 17.45. Found: C, 10.89; N, 26.09; K, 12.09; Fe, 17.48. Calcd for $K[Co(H_2N'{-}NH{-}COO)_3]$: C, 11.15; N, 26.01; K, 12.10; Co, 18.24. Found: C, 11.33; N, 26.14; K, 12.09; Co, 18.15. Calcd for $K[Ni(H_2N'{-}NH{-}COO)_3]$: C, 11.16; N, 26.03; K, 12.11; Ni, 18.18. Found: C, 11.15; N, 26.11; K, 11.92; Ni, 18.29. Calcd for $K[Zn(H_2N'{-}NH{-}COO)_3]$: C, 10.93; N, 25.50; K, 11.86; Zn, 19.83. Found: C, 11.09; N, 25.80; K, 11.94; Zn, 19.44.

(c) The compounds bis(hydrazinecarboxylato-N′,O)metal(II) dihydrate, $Co(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$ and $Ni(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$, were obtained by dissolving the tris chelates (see (iii) (a)) in water; after several days the crystals were separated by hydrolysis. The two compounds are not isostructural.[26] *Anal.* Calcd for $Co(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$: N, 22.86; Co, 24.05. Found: N, 22.98; Co, 24.08. Calcd for $Ni(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$: N, 22.88; Ni, 23.98. Found: N, 22.69; Ni, 23.90.

(d) The compounds bis(hydrazinecarboxylato-N′,O)manganese(II) dihydrate, $Mn(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$, bis(hydrazinecarboxylato-N′,O)magnesium dihydrate, $Mg(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$, and bis(hydrazinecarboxylato-N′,O)cadmium monohydrate, $Cd(H_2N'{-}NH{-}COO)_2\cdot H_2O$, were obtained from aqueous solutions of the metal salt added to hydrazine hydrate and carbon dioxide.[26] No tris complex has been obtained with these cations. The manganese compound is isostructural with both the magnesium and cobalt compounds. *Anal.* Calcd for $Mn(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$: N, 23.24; Mn, 22.79. Found: N, 23.34; Mn, 22.73. Calcd for $Mg(H_2N'{-}NH{-}COO)_2\cdot 2H_2O$: N, 26.63; Mg, 11.87. Found: N, 27.06; Mg, 11.56. Calcd for $Cd(H_2N'{-}NH{-}COO)_2\cdot H_2O$: N, 40.07; Cd, 19.97. Found: N, 39.80; Cd, 20.16.

(e) The compound calcium dihydrazinecarboxylate monohydrate, $Ca(H_2N'{-}NH{-}COO)_2\cdot H_2O$, was obtained from an aqueous solution of calcium acetate by addition of very small amounts of hydrazine hydrate and carbon dioxide. The crystals are colorless and monoclinic. *Anal.* Calcd for $Ca(H_2N'{-}NH{-}COO)_2\cdot H_2O$: N, 26.92; Ca, 19.25. Found: N, 27.15; Ca, 19.28.

All the compounds of each isostructural set were checked also by powder photographs.

Infrared Spectra.—Infrared spectra were obtained with a Perkin-Elmer spectrophotometer, Model 137. Nearly all of the spectra were taken with KBr disks, except the spectra of nitrates and of hydrazinecarboxylic acid, for which Nujol mulls were employed. In the following list hyc stands for the hydrazinecarboxylato group, $H_2N'{-}NH{-}COO$, –Y indicates –COO or –CSS, and the frequencies are in cm^{-1}.

ν(N–N) in unidentate $H_2N{-}NH_2$: $Co(N_2H_4)_2(hyc)_2$, 933; $Ni(N_2H_4)_2(hyc)_2$, 936; $Zn(N_2H_4)_2(hyc)_2$, 931. ν(N–N) in bridging $H_2N{-}NH_2$: $[Mn(N_2H_4)_2]Cl_2$, 964; $[Fe(N_2H_4)_2]Cl_2$, 968; $[Co(N_2H_4)_2]Cl_2$, 976; $[Ni(N_2H_4)_2]Cl_2$, 980; $[Zn(N_2H_4)_2]Cl_2$, 980; $[Cd(N_2H_4)_2]Cl_2$, 968; $[Mn(N_2H_4)_2]Br_2$, 957; $[Zn(N_2H_4)_2]Br_2$, 971; $[Cd(N_2H_4)_2]Br_2$, 961; $[Mn(N_2H_4)_2]I_2$, 948;

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$[Zn(N_2H_4)_2]I_2$, 957; $[Cd(N_2H_4)_2]I_2$, 952; $[Mn(N_2H_4)_2](NCS)_2$, 957; $[Fe(N_2H_4)_2](NCS)_2$, 962; $[Co(N_2H_4)_2](NCS)_2$, 969; $[Ni(N_2H_4)_2](NCS)_2$, 976; $[Zn(N_2H_4)_2](NCS)_2$, 971; $[Cd(N_2H_4)_2](NCS)_2$, 962; $[Mn(N_2H_4)_2](CH_3COO)_2$, 963; $[Zn(N_2H_4)_2](CH_3COO)_2$, 978; $[Cd(N_2H_4)_2](CH_3COO)_2$, 968; $[Mn(N_2H_4)_3](NO_3)_2$, 964; $[Co(N_2H_4)_3](NO_3)_2$, 975; $[Ni(N_2H_4)_3](NO_3)_2$, 978; $[Zn(N_2H_4)_3](NO_3)_2$, 975; $[Cd(N_2H_4)_3](NO_3)_2$, 969. ν(N–N) in $H_2N{-}NH_3^+$ cation: $(N_2H_5)_2CdCl_4$, 960; $(N_2H_5)_3CdCl_5$, 962; $(N_2H_5)[Fe(hyc)_3]\cdot H_2O$, 962; $(N_2H_5)[Co(hyc)_3]\cdot H_2O$, 962; $(N_2H_5)[Ni(hyc)_3]\cdot H_2O$, 965; $(N_2H_5)[Zn(hyc)_3]\cdot H_2O$, 958; $(N_2H_5)(N'H_2{-}NH{-}CSS)$,963. ν(N–N) in $H_2N'{-}NH{-}Y$: $NH_2{-}NHCOOH$, 998; $Co(N_2H_4)_2(hyc)_2$, 990; $Ni(N_2H_4)_2(hyc)_2$, 995; $Zn(N_2H_4)_2(hyc)_2$, 992; $(N_2H_5)[Fe(hyc)_3]\cdot H_2O$, 995; $(N_2H_5)[Co(hyc)_3]\cdot H_2O$, 990; $(N_2H_5)[Ni(hyc)_3]\cdot H_2O$, 995; $(N_2H_5)[Zn(hyc)_3]\cdot H_2O$, 992; $K[Fe(hyc)_3]$, 1002; $K[Co(hyc)_3]$, 998; $K[Ni(hyc)_3]$, 1003; $K[Zn(hyc)_3]$, 1000; $Mg(hyc)_2\cdot 2H_2O$, 1001; $Mn(hyc)_2\cdot 2H_2O$, 998; $Co(hyc)_2\cdot 2H_2O$, 998; $Ni(hyc)_2\cdot 2H_2O$, 1013; $Cd(hyc)_2\cdot H_2O$, 992; $Ca(hyc)_2\cdot H_2O$, 995; $(N_2H_5)(N'H_2{-}NHCSS)$, 986.

Crystal Data.—The crystal data were determined from rotation and Weissenberg photographs (Cu Kα radiation, λ 1.5418 Å), except those for $[Mn(N_2H_4)_2]Br_2$. A powder diffractogram was indexed by comparison with the diffractogram of the isostructural chloride and iodide compounds; then the unit cell constants were refined by a least-squares method using the computer Olivetti Elea 6001/S of Centro di Calcolo Elettronico of the University of Parma.

Discussion

The stretching band ν(N–N) can be assigned on the basis of preceding works.[27–31] In the compounds examined, ν(N–N) can be found at the frequency ranges: (A) 931–936 cm^{-1} in unidentate $H_2N{-}NH_2$ (see Figure 1a), (B) 948–980 cm^{-1} in bridging $H_2N{-}NH_2$ (see Figure 1b), (C) 958–965 cm^{-1} in the cation $H_2N{-}NH_3^+$ (see Figure 1e, f), (D) 986–1013 cm^{-1} in $H_2N{-}NH{-}Y$ (see Figure 1a, c, d, e). The hydrazine molecule in the solid shows ν(N–N) at 885 cm^{-1} [28] and the cation $^+H_3N{-}NH_3^+$ at 1024 cm^{-1}.[28]

The trend of ν(N–N) reflects the diminishing or increasing repulsion between lone pairs. Whenever the stretching frequency increases, there correspond bands implying interaction, either by conjugation or by field effect, of one lone pair or both with the residual of the molecule. In fact, all of the stretching frequencies observed are greater than ν(N–N) = 885 cm^{-1} of the solid hydrazine. Moreover (νN–N) for unidentate $H_2N{-}NH_2$ is smaller than for bridging $H_2N{-}NH_2$, and that for $H_2N{-}NH_3^+$ is smaller than for $^+H_3N{-}NH_3^+$.

If the hydrazine radical $H_2N'{-}NH{-}$ is attached to a conjugate system (–COO, –CSS), then ν(N–N) increases up to 980–1000 cm^{-1}, either if the resulting group is chelating or not. The increase is in accordance with the X-ray diffraction studies,[6,9–11,32] which show how the atoms NCOO or NCSS, but not in general N′, lie in the same plane and form a conjugate system. The distinction between chelating and nonchelating hydrazinecarboxylato groups seems only possible from the broadening of the band in the chelates.

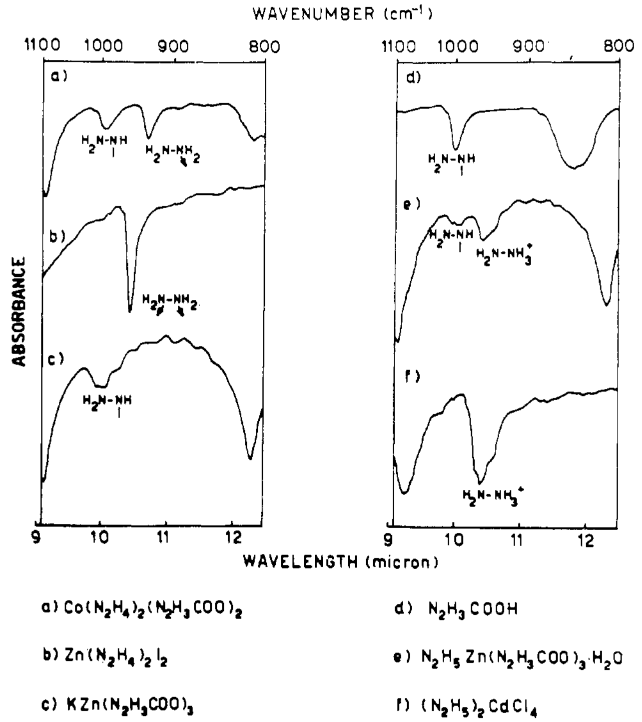


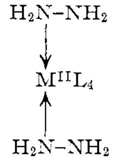
Figure 1.—Portions of typical vibrational spectra of compounds and derivatives of hydrazine, with nitrogen–nitrogen stretching bands.

TABLE I

REPEAT DISTANCE c AND STRETCHING FREQUENCY ν(N–N) IN CHAIN COMPLEXES WITH N_2H_4 BRIDGING

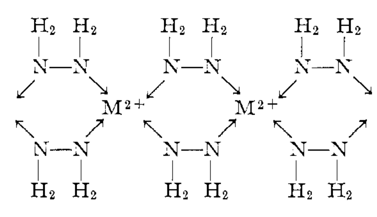
Compound	c, Å	ν, cm^{-1}	Compound	c, Å	ν, cm^{-1}
$[Zn(N_2H_4)_2]Cl_2$	4.13	980	$[Mn(N_2H_4)_2](NCS)_2$	4.37	957
$[Zn(N_2H_4)_2](CH_3COO)_2$	4.14	978	$[Mn(N_2H_4)_2]I_2$	4.41	948
$[Zn(N_2H_4)_2]Br_2$	4.18	971	$[Cd(N_2H_4)_2]Cl_2$	4.33	968
$[Zn(N_2H_4)_2](NCS)_2$	4.21	971	$[Cd(N_2H_4)_2](CH_3COO)_2$	4.33	968
$[Zn(N_2H_4)_2]I_2$	4.51	957	$[Cd(N_2H_4)_2]Br_2$	4.44	961
$[Mn(N_2H_4)_2]Cl_2$	4.29	964	$[Cd(N_2H_4)_2](NCS)_2$	4.41	962
$[Mn(N_2H_4)_2](CH_3COO)_2$	4.28	963	$[Cd(N_2H_4)_2]I_2$	4.52	952
$[Mn(N_2H_4)_2]Br_2$	4.32	957			

Although the nitrogen–nitrogen bond distance remains unaltered, the nitrogen–nitrogen stretching band in the complexes of unidentate hydrazine



$$\begin{array}{c} H_2N{-}NH_2 \\ \downarrow \\ M^{II}L_4 \\ \uparrow \\ H_2N{-}NH_2 \end{array}$$

is found at lower frequencies (ν(N–N) = 931 cm^{-1} for the zinc compound) than in the chain complexes



with bridging hydrazine molecules (ν(N–N) = 980 cm^{-1} for the zinc chloride compound), in accordance with the

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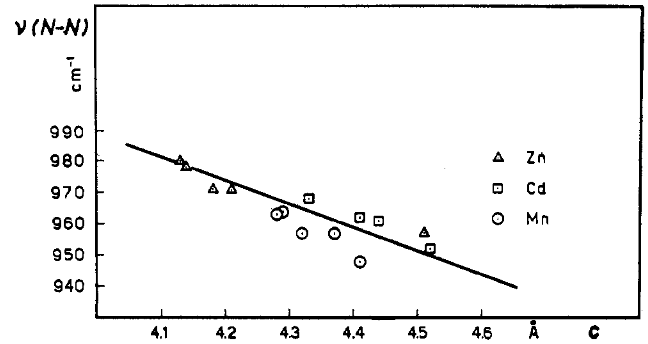

Figure 2.—Relation between stretching band frequency ν (N–N) and repeat distance *c* in chain complexes $[M^{II}(N_2H_4)_2]_nX_{2n}$.

increased field effect, in the latter, of the positive cations on the lone pairs. Even the small shifts within the set of the chain complexes (Table I) can be related to changing of the repulsion between lone pairs, owing to the electrostatic field effect of the cations. In this set of compounds ν(N–N) is inversely proportional (Figure 2) to the repeat distance along the chain; *i.e.*, the larger is the distance of the attractive positive charges, the weaker is the field effect on the lone pairs.

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Coordination Chemistry of 4,4'-Bipyridine[1,2]

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Complexes of 4,4'-bipyridine with Ag(I), Hg(II), Co(II), Cu(II), and Ni(II) have been prepared. Physical properties, stoichiometries, diffuse reflectance spectra, and infrared spectral data indicate that the compounds are coordination polymers in which the ligand acts as a bridging group. Also, the basicity of the ligand has been determined as a function of ionic strength. Acid dissociation constants of quaternized 4,4'-bipyridine are: $K_1 = 6.5 \times 10^{-4}$, 4.9×10^{-4}, and 3.5×10^{-4}; $K_2 = 1.4 \times 10^{-5}$, 1.4×10^{-5}, and 1.2×10^{-5} at molar ionic strengths 0.05, 0.10, and 0.20, respectively.

Introduction

The chemistry of polymeric transition metal complexes is in its infancy. The coordination chemistry of 2,2'-bipyridine has been extensively studied, yet the ligand properties of the isomeric 4,4'-bipyridine molecule have not been investigated. The only references to transition metal–4,4'-bipyridine complexes appear in papers by Peard and Pflaum,[3] who report a compound having the stoichiometric formula $Ag(C_{10}H_8N_2)(NO_3)$, and by Lewis and Mabbs,[4] who report a compound of copper(II) benzoate containing half a 4,4'-bipyridine molecule per formula unit of copper benzoate. As a potential ligand, 4,4'-bipyridine seemed particularly interesting because its structure should preclude chelation and favor coordination of the nitrogen atoms to two different metal ions; *i.e.*, it should coordinate so as to form polymeric complexes. This work was undertaken to determine the basicity of 4,4'-bipyridine as a function of ionic strength and to prepare and characterize 4,4'-bipyridine complexes of transition metal ions.

Experimental Section

Materials.—A modification of the method of Dimroth and Frister[5] was used to prepare 4,4'-bipyridine. Pyridine (50 ml, dried over phosphorus pentoxide), 250 ml of acetic anhydride, and 50 g of zinc dust were stirred together for 2 hr. The yellow precipitate formed was dissolved as completely as possible by heating the mixture on a steam bath for 2 hr. The liquid was filtered off and allowed to crystallize under refrigeration. The yellow crystalline product was then collected by filtration and allowed to oxidize in air for 2–4 days, during which white crystals of 4,4'-bipyridine appeared on the surface of the yellow-brown mixture. The entire mass was then added to 200 ml of water, made slightly acid with hydrochloric acid, and the resulting solution was filtered while hot. The clear filtrate was made basic with sodium hydroxide and set aside on an ice bath to allow crystallization to occur. Recrystallization was repeated until a pure white product was obtained. The yield was approximately 50% based upon pyridine. Other chemicals were reagent grade.

Measurements.—A Sargent Model DR high-precision pH meter equipped with a combination glass–calomel electrode was used for all pH measurements.

Diffuse reflectance spectra were obtained with a Beckman DU spectrophotometer equipped with a No. 2580 diffuse reflectance attachment. A 1-in. magnesium carbonate reference block was used for standardization.

A Perkin-Elmer Model 337 grating infrared spectrophotometer was used to determine infrared spectra.

Analyses.—Cobalt, nickel, and copper were determined by conventional complexometric titration with EDTA. Mercury(II) was determined by thiocyanate titration to a ferric ion end point, and silver(I) was determined gravimetrically by precipitation as silver chloride. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories of Knoxville, Tenn.

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