However, whichever mechanism is operative, two pentacyanocobalt ions must come close together. The lack of reaction in the present system may indicate that this approach is not possible because of the bulkiness of the tetraalkylammonium cations. This effect may also rationalize two other major differences between the two systems. First, compounds I show no tendency to dimerize either in concentrated solution or in the solid state. In fact, analogs of the compounds $M_6[Co_2(CN)_{10}]\cdot xH_2O$ have not been observed in the present system, whereas all previous attempts to obtain the monomeric ion, except the one report of Pregaglia and coworkers,[12] have given these dimers. It is notable that lithium is the cation in the one previous exception. The high charge/radius ratio of this ion promotes ion pairing which might hinder dimerization. Also, the acetone and ethanol observed in their product are most probably associated with the cation, thus giving it a large effective size and, thereby, further obstructing close approach of two anions. Secondly, the solutions of I in acetonitrile and of II in water differ in their reaction with oxygen in that, in the latter case, the dinuclear complex ion $[(CN)_5CoOOCo(CN)_5]^{6-}$ is produced,[44] whereas in the former the reaction stops at $[Co(CN)_5O_2]^{3-}$, which has been observed[44] as an intermediate in the formation of the dinuclear complex. Again, the lack of formation of a dinuclear complex may be attributed to the inability of two ions to come in close contact due to the bulkiness of the cations.

Although the ion $[Co(CN)_5H]^{3-}$ is not obtainable by reaction of Ia with hydrogen, it is formed on electrochemical reduction of its aqueous solutions. It is notable that in this case the mechanism consists of addition of an electron followed or accompanied by a bimolecular reaction with water; *i.e.*, it does not require close approach of two anions.

We have observed that acetonitrile solutions of Ia react with benzoquinone to give dark diamagnetic solutions, presumably containing benzoquinone-bridged anions reported by Vlček and Hanzlik.[56] Diamagnetic solutions were also obtained on reaction with halogens and with allylic halides in acetonitrile, again suggesting reactions similar to those observed[6] for aqueous solutions of II.

Acknowledgments.—The authors are indebted to Professor F. C. Anson for the preprints of two papers on the pentacyanocobalt(II) ion and for the loan of a copy of Matschiner's thesis,[31] to Dr. M. Takano for a translation of a paper[28] in Japanese, and to Dr. P. A. Berger for running the esr spectra.

[56] A. A. Vlček and J. Hanzlík, *Inorg. Chem.*, **6**, 2053 (1967).

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Ionization Equilibria in Anhydrous Cobalt(II) Chloride–Acetonitrile

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Independent investigators have studied the anhydrous $CoCl_2$–CH_3CN system and have arrived at somewhat ambiguous results. Janz and coworkers have proposed the existence of a neutral dimer, $(CoCl_2\cdot 3L)_2$, which dissociates into CoL_6^{2+} and $CoCl_4^{2-}$, where L = CH_3CN. Libus and coworkers denied the existence of dimeric species and proposed that dissociation produces CoL_6^{2+} and $CoCl_3L^-$, where again L = CH_3CN. In the present investigation, effective molecular weights and visible absorption spectra indicate that the ionic dimer $(CoCl_3^-)_2$ is formed in significant amounts in the system. It is also observed that the formation of this dimeric species is facilitated by the addition of salts such as Et_4NCl or LiCl that furnish additional chloride ions to the acetonitrile medium and that the dimerization is independent of the size of the cation associated with the added chloride salt.

Introduction

The anhydrous system composed of $CoCl_2$ and CH_3CN has been studied by independent investigators in an attempt to identify the ionic and molecular species in the system and also to establish the nature of the equilibrium processes responsible for the existence of these species. On the basis of electrical conductance data, solid substrate analysis, and visible absorption spectra, Janz[1] proposed the following model as a description of the ionization processes operating in the anhydrous system, where L = CH_3CN

$$2CoCl_2 + 6L \rightleftharpoons (CoL_6^{2+}CoCl_4^{2-}) \qquad (1)$$

$$(CoL_6^{2+}CoCl_4^{2-}) \rightleftharpoons CoL_6^{2+} + CoCl_4^{2-} \qquad (2)$$

$$(CoL_6^{2+}CoCl_4^{2-}) + 2L \rightleftharpoons CoL_6^{2+} + CoCl_4L_2^{2-} \qquad (3)$$

In a separate study, Libus[2] concluded, on the basis of visible absorption spectra, that the following model is a better description of the system where again L = CN_3CN

$$CoCl_2 + 2L \rightleftharpoons CoCl_2L_2 \qquad (4)$$

$$3CoCl_2L_2 + 2L \rightleftharpoons CoL_6^{2+} + 2CoCl_3L^- \qquad (5)$$

The basic differences in these two models lie in the fact that a dimeric species was proposed by Janz, while no monomer–dimer equilibrium was predicted by Libus, and in the fact that Janz identified the major anionic species present as $CoCl_4^{2-}$, while Libus reported the predominant anion as $CoCl_3L^-$.

In the present investigation, the apparent molecular weight of $CoCl_2$ in CH_3CN is determined by vapor pressure osmometry, in both the presence and absence of additional chloride ion. These data are correlated with visible absorption spectra in an attempt to reconcile the controversy surrounding the existence of a monomer–dimer equilibrium and to provide further

[1] G. J. Janz, A. E. Marcinkowsky, and H. V. Venkatasetty, *Electrochim. Acta*, **8**, 867 (1963).

[2] W. Libus, *Rocz. Chem.*, **36**, 999 (1962).

information about the nature of the anionic species present in this system.

Experimental Section

Materials.—Anhydrous CH_3CN was prepared according to the procedures reported by Libus and Puchalska.[3]

Anhydrous $CoCl_2$ was prepared from reagent grade hexahydrate by preliminary drying under vacuum, first at a temperature of 80° and then, after being ground into a fine powder, at 150°. Final drying was carried out at 200° under a screen of dry HCl gas. The salt was then degassed under vacuum over KOH and stored under an atmosphere of dry nitrogen. The salt prepared in this manner was analyzed by potentiometric silver nitrate titration and found to be 100 ± 0.3% $CoCl_2$.

Benzil was purified by procedures reported by Richtol and Belorit.[4] Et_4NCl was purified as described by Padova and Abrahamer.[5] Reagent grade LiCl was dried at 115° and used without further purification.

Et_4NCoCl_3, a 1:1 complex salt of Et_4NCl and $CoCl_2$, was prepared from the reagents described above by the following procedure. Equimolar amounts of $CoCl_2$ and Et_4NCl were dissolved in anhydrous CH_3CN and the solvent was partially removed under vacuum. The concentrated solution was cooled to −20° and the resulting dark purple precipitate was collected on a glass filter. The product was washed with cold (−20°) solvent and dried under vacuum at 150°. The compound prepared in this manner exhibited a melting point range of 165–166°, and elemental analysis showed the empirical formula to be $C_8H_{20}NCoCl_3$. The numerical results of this analysis were as follows: 31.67% C, 7.27% H, 4.62% N, 20.80% Co, 35.64% Cl.

The fact that the material isolated according to these procedures is indeed a stable complex salt is evidenced by its stability in the presence of water vapor. Upon exposure to moist air the salt retains its blue-violet color and appears to be only slightly hygroscopic. Simple mixtures of anhydrous $CoCl_2$ and Et_4NCl would not be expected to exhibit this type of behavior.

Apparatus and Procedures.—Molecular weight values were determined on Mechrolab Model 301 and Hewlett-Packard Model 302 vapor pressure osmometers. Both instruments were thermostated at 37° and calibrated with purified benzil.

Absorption spectra were determined on a Cary Model 14 recording spectrophotometer using cells of 10-, 1.0-, and 0.10-path lengths.

All solutions were prepared by weight under an atmosphere of dry nitrogen.

Results and Discussion

$CoCl_2$ in CH_3CN.—The effective molecular weight of $CoCl_2$ in CH_3CN was measured as a function of concentration and the results are presented in Table I. These results indicate the existence of some type of monomer–dimer equilibrium with the amount of dimer present becoming more significant as the formal solution concentration is increased. Visible absorption spectra of the same system are presented in Figures 1 and 2. These spectra show that, as the formal solution concentration is increased, the absorption bands at 575 and 615 mμ, which Libus has attributed to $CoCl_2L_2$, gradually lose prominence while the absorption band at 590 mμ, previously attributed to $CoCl_3L^-$, regularly increases in intensity. These spectral changes and the effective molecular weight values indicate the existence of a concentration-dependent process in which the neutral monomeric species $CoCl_2$ is at least partially converted to the ionic dimer $(CoCl_3^-)_2$. This process can be formulated as follows, where L = CH_3CN

TABLE I

MOLECULAR WEIGHT CONCENTRATION DEPENDENCE OF COBALT(II) CHLORIDE IN ACETONITRILE

10^2C, *m*	Mol wt	Mol wt/ form. wt	10^2C, *m*	Mol wt	Mol wt/ form. wt
1.00	123	0.947	7.00	175	1.35
2.00	150	1.16	8.00	177	1.36
3.00	161	1.24	9.00	179	1.38
4.00	167	1.29	10.0	180	1.39
5.00	172	1.32	20.0	182	1.40
6.00	174	1.34	30.0	184	1.42

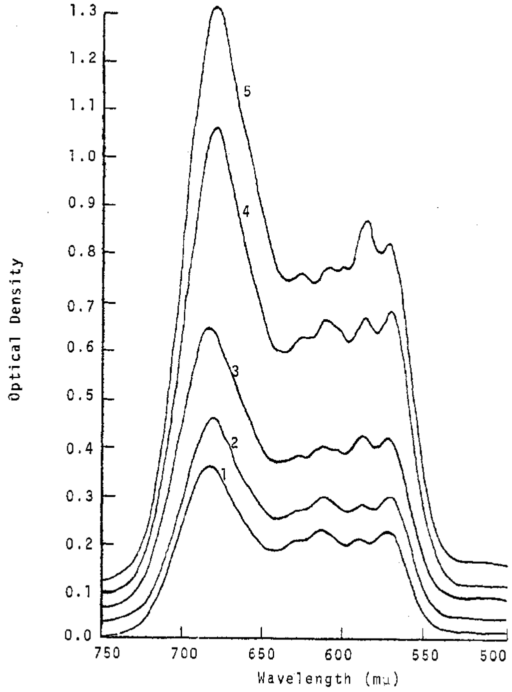

Figure 1.—Absorption spectra of $CoCl_2$ in acetonitrile (1.0-mm path length). Molal $CoCl_2$ concentrations: (1) 1.19×10^{-2}; (2) 1.40×10^{-2}; (3) 1.91×10^{-2}; (4) 3.19×10^{-2}; (5) 4.05×10^{-2}.

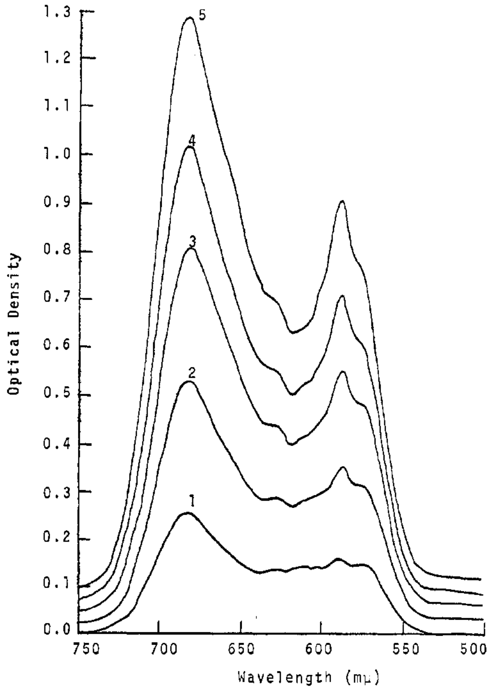

Figure 2.—Absorption spectra of $CoCl_2$ in acetonitrile (0.10-mm path length). Molal $CoCl_2$ concentrations: (1) 7.95×10^{-2}; (2) 1.62×10^{-1}; (3) 2.38×10^{-1}; (4) 3.04×10^{-1}; (5) 4.09×10^{-1}.

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[3] W. Libus and D. Puchalska, *J. Phys. Chem.*, **71**, 3549 (1967).

[4] H. H. Richtol and A. Belorit, *J. Chem. Phys.*, **45**, 35 (1966).

[5] J. Padova and I. Abrahamer, *J. Phys. Chem.*, **71**, 2112 (1967).

$$3CoCl_2 + 6L \rightleftharpoons CoL_6^{2+} + (CoCl_3^-)_2 \qquad (6)$$

It should be noted at this point that the number of solvent molecules attached to the ionic dimer $(CoCl_3^-)_2$ is uncertain and that the formula should be more properly written $(Co_2Cl_6 \cdot uL)^{2-}$.

1:1 Molar Mixtures of $CoCl_2$ and Et_4NCl.—The effective molecular weight of 1:1 molar mixtures of $CoCl_2$ and Et_4NCl was measured as a function of concentration and the results are presented in Table II. These results are interpreted by means of a comparison study in which the experimental molecular weights and their concentration dependences are compared with the molecular weight behavior which would theoretically result from the various possible chemical interactions that could take place between the two solutes. The results of this comparison study are presented in Table III which shows each possible solute interaction and the theoretical molecular weight behavior that would be expected to result from such an interaction if it were an accurate description of the system. If no interaction takes place between the two solutes and no dimerization occurs, as indicated by either eq B or eq C, the effective molecular weight would not be expected to be a function of concentration as is actually observed. Also the magnitude of the molecular weight corresponding to eq B or C is significantly lower than that actually observed. Equation C also assumes that Et_4NCl is not appreciably ionized in CH_3CN, an unlikely prospect in light of conductance data reported by Walden and Birr.[6] For the same reason, eq D, in which a neutral dimer is formed, is also questionable, even though the theoretical molecular weight is in good agreement with the experimental values. Equation E, in which a neutral dimer is formed in the presence of ionized Et_4NCl, and eq F, in which the monomeric $CoCl_3^-$ ion is produced, are also discarded by reason of their low theoretical molecular weight values.

TABLE II

MOLECULAR WEIGHT CONCENTRATION DEPENDENCE OF 1:1 MOLAR MIXTURES OF $CoCl_2$ AND Et_4NCl IN ACETONITRILE

10^2C,[a] m	Eff mol wt	10^2C,[a] m	Eff mol wt	10^2C,[a] m	Eff mol wt
1.00	145	4.00	179	7.00	185
2.00	166	5.00	183	8.00	186
3.00	175	6.00	184	9.00	187
				10.0	189

[a] Formal concentration of $CoCl_2$ which is equal to the formal concentration of Et_4NCl.

TABLE III

THEORETICAL MOLECULAR WEIGHTS FOR POSSIBLE SOLUTE INTERACTIONS IN THE $CoCl_2$–Et_4NCl SYSTEM[a]

	Theoretical interaction	Eff mol wt
A.	$2CoCl_2 + 2Et_4N^+ + 2Cl^- \rightleftharpoons 2Et_4N^+ + (CoCl_3^-)_2$	197
B.	$CoCl_2 + Et_4N^+ + Cl^- \rightarrow$ no interaction	99
C.	$CoCl_2 + Et_4NCl \rightarrow$ no interaction	148
D.	$2CoCl_2 + 2Et_4NCl \rightleftharpoons 2Et_4NCl + (CoCl_2)_2$	197
E.	$2CoCl_2 + 2Et_4N^+ + 2Cl^- \rightleftharpoons 2Et_4N^+ + 2Cl^- + (CoCl_2)_2$	118
F.	$CoCl_2 + Et_4N^+ + Cl^- \rightleftharpoons Et_4N^+ + CoCl_3^-$	148

[a] In all equilibrium interactions the theoretical molecular weight is based upon the assumption that the equilibrium is essentially displaced to the right.

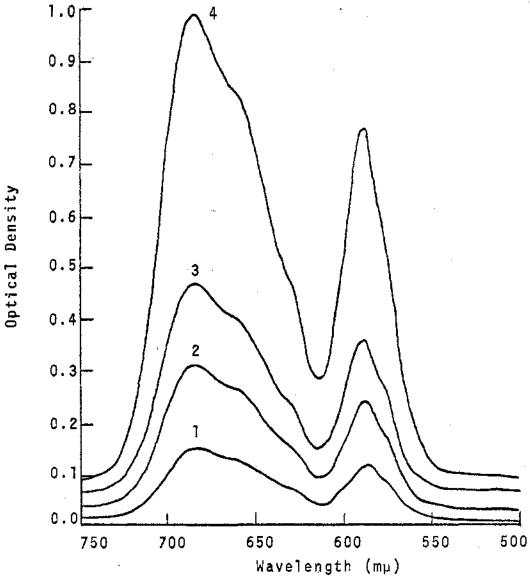

Figure 3.—Absorption spectra of 1:1 molar mixtures of $CoCl_2$ and Et_4NCl in acetonitrile (1.0-mm path length). Molal $CoCl_2$ concentrations: (1) 3.34×10^{-3}; (2) 6.97×10^{-3}; (3) 1.00×10^{-2}; (4) 2.23×10^{-2}.

It can be concluded from the above discussion that the only theoretical interaction in good agreement with the experimental molecular weight values is given by eq A in which an ionic dimer, $(CoCl_3^-)_2$, is formed by a chloride ion transfer from Et_4NCl to $CoCl_2$ and dimerization.

Representative absorption spectra of the same system are presented in Figure 3. These spectra show no significant change in the number or position of absorption bands as the solution concentration is increased from 3.34×10^{-3} to 3.03×10^{-1} *m*. This behavior is consistent with the molecular weight data which indicate that significant dimerization occurs in these solutions, even at relatively low concentrations. Even more interesting is the fact that the absorption spectrum of a 1:1 molar mixture of $CoCl_2$ and Et_4NCl at any concentration is essentially identical with the spectrum exhibited by $CoCl_2$ at higher concentrations in the absence of added chloride ion. This spectral identity can be taken as further evidence of the postulated equilibrium described by eq 6.

Et_4NCoCl_3.—The complex salt isolated from 1:1 molar mixtures of $CoCl_2$ and Et_4NCl was subjected to molecular weight determinations and the results are presented in Table IV. If this complex salt ionizes completely according to the equation

$$2Et_4NCoCl \longrightarrow 2Et_4N^+ + (CoCl_3^-)_2$$

TABLE IV

MOLECULAR WEIGHT CONCENTRATION DEPENDENCE OF Et_4NCoCl_3

10^2C, m	Eff mol wt	10^2C, m	Eff mol wt	10^2C, m	Eff mol wt
2.00	191	12.0	191	22.0	191
4.00	193	14.0	192	24.0	191
6.00	192	16.0	191	26.0	190
8.00	193	18.0	191	28.0	190
10.0	191	20.0	191	30.0	192

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[6] P. Walden and E. J. Birr, *Z. Phys. Chem., Abt. A*, **144**, 269 (1929).

TABLE V

MOLECULAR WEIGHT CONCENTRATION DEPENDENCE OF 1:1 MOLAR MIXTURES OF $CoCl_2$ AND LiCl IN ACETONITRILE

10^2C,[a] *m*	Eff mol wt	10^2C,[a] *m*	Eff mol wt	10^2C,[a] *m*	Eff mol wt
1.00	91.0	4.00	102	7.00	104
2.00	97.5	5.00	103	8.00	104
3.00	101	6.00	104		

[a] Formal concentration of $CoCl_2$ which is equal to the formal concentration of LiCl.

TABLE VI

THEORETICAL MOLECULAR WEIGHTS FOR POSSIBLE SOLUTE INTERACTIONS IN THE $CoCl_2$–LiCl SYSTEM[a]

	Theoretical interaction	Eff mol wt
A.	$2CoCl_2 + 2Li^+ + 2Cl^- \rightleftarrows 2Li^+ + (CoCl_3^-)_2$	115
B.	$CoCl_2 + Li^+ + Cl^- \rightarrow$ no interaction	57
C.	$CoCl_2 + LiCl \rightarrow$ no interaction	86
D.	$2CoCl_2 + 2LiCl \rightleftarrows 2LiCl + (CoCl_2)_2$	115
E.	$2CoCl_2 + 2Li^+ + 2Cl^- \rightleftarrows 2Li^+ + 2Cl^- + (CoCl_2)_2$	69
F.	$CoCl_2 + Li^+ + Cl^- \rightleftarrows Li^+ + CoCl_3^-$	86

[a] In all equilibrium interactions, the theoretical molecular weight is based upon the assumption that the equilibrium is essentially displaced to the right.

the system would be expected to exhibit a theoretical effective molecular weight of 197 which would be essentially independent of the formal solution concentration. The results presented in Table III confirm this prediction and give further evidence that it is possible for $(CoCl_3^-)_2$ to exist in these acetonitrile solutions. It should be noted at this point that an apparent inconsistency exists in the concentration dependence of the effective molecular weight of 1:1 molar mixtures of Et_4NCl and $CoCl_2$ and the complex salt Et_4NCoCl_3. At the present time, no satisfactory explanation can be made adequately to account for this difference in the behavior of these two systems which should be chemically equivalent.

Absorption spectra of the Et_4NCoCl_3–CH_3CN system were determined and it was found that these complex salt solutions, like the 1:1 molar mixtures described above, exhibit spectra which are essentially identical with those generated in concentrated $CoCl_2$ solutions. This spectral identity lends even more support to the proposed dimerization process described by eq 6.

1:1 Molar Mixtures of $CoCl_2$ and LiCl.—A molecular weight and spectral study, similar to that carried out on 1:1 molar mixtures of $CoCl_2$ and Et_4NCl, was made on 1:1 molar mixtures of $CoCl_2$ and LiCl. The results of the molecular weight study are presented in Tables V and VI, and the absorption spectra of this system were found to be essentially identical with those presented in Figure 3 for 1:1 molar mixtures of $CoCl_2$ and Et_4NCl. By an interpretation analogous to that of the $CoCl_2$–Et_4NCl system, it can be concluded that similar interactions take place in the system composed of $CoCl_2$ and LiCl and that the formation of the ionic dimer $(CoCl_3^-)_2$ is not significantly affected by the size of the cation corresponding to the added chloride salt.

In conclusion, we wish to point out that while the data presented in this paper are consistent with the model described by eq 6, the absolute identification of complex ionic species in solution remains a very difficult task. Consequently, we cannot absolutely rule out certain other possibilities that might also be consistent with the data presented here.

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Double Isopropoxides of Aluminum, Gallium, and Indium

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A number of double isopropoxides of aluminum, gallium, and indium with the general formula $M\{M'(i\text{-PrO})_4\}_3$ have been prepared by the reactions of the anhydrous chloride of one metal with the required quantity of potassium aluminum (or gallium) tetraisopropoxide or by refluxing together the two isopropoxides. The products are volatile under reduced pressure and can be recrystallized unchanged; they show molecular weights corresponding to the formula weights in benzene. Ir and nmr spectra have been recorded; the latter have been particularly useful in elucidating the structures of these new products.

Introduction

The pioneering work of Meerwein and Bersin[1] on double alkoxides appears to indicate that the combinations of strongly basic and acidic alkoxides generally tend to give stable "double alkoxo salts." The stability of a number of double alkoxides of lanthanide elements (La, Pr,[2] Nd, Sm, Dy, Yb, Y[3]) with aluminum and gallium recently synthesized in these laboratories is understandable from the above point of view. It has, therefore, been considered worthwhile to investigate whether the weakly basic elements aluminum, gallium, and indium tend to form double alkoxy species among themselves also.

Results

The synthesis of double isopropoxides of indium with aluminum and gallium has been carried out by reaction of anhydrous indium chloride with potassium, aluminum, or gallium tetraisopropoxide in 1:3 ratio in isopropyl alcohol

$$InCl_3 + 3KM(i\text{-PrO})_4 \longrightarrow In\{M(i\text{-PrO})_4\}_3 + 3KCl$$
$$M = Al \text{ or } Ga$$

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[1] H. Meerwein and T. Bersin, *Justus Liebigs Ann. Chem.*, **476**, 113 (1929); *Chem. Abstr.*, **24**, 586 (1930).

[2] R. C. Mehrotra and M. M. Agarwal, *Chem. Commun.*, 469 (1968).

[3] M. M. Agarwal, Ph.D. Thesis, University of Rajasthan, Jaipur, 1968.