

Easily recyclable polymeric V(V) salen complex for the enantioselective *O*-acetyl cyanation of aldehydes

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Abstract

A new recyclable polymeric V(V) salen complex **1** derived from poly[(*R,R*)-*N,N'*-bis-{3-(1,1-dimethylethyl)-5-methylene salicylidene} cyclohexane 1,2-diamine] with vanadyl sulphate was synthesized and characterized by microanalysis, ¹H NMR, optical rotation, IR, and UV–vis spectroscopy. The complex **1** was used as catalyst for asymmetric *O*-acetyl cyanation of various aldehydes with KCN as an inexpensive and non-volatile cyanide source and acetic anhydride at –20 °C. High chiral induction (ee, 96%) for *O*-acetylcyanohydrin was obtained in the case of 2-methylbenzaldehyde with added advantage of catalyst recyclability.

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1. Introduction

Asymmetric cyanohydrin synthesis is attracting significant interest in recent years largely due to their potential applications in pharmaceuticals, agrochemicals and other fields. Consequently, many efficient and successful synthetic methods have been developed, however, the chiral catalytic method is one of the most attractive strategy where asymmetric addition of a cyanide to the carbonyl group of aldehydes and ketones was affected with the help of a catalyst among enzymes [1], synthetic peptides [2], organocatalysts [3] or transition metal complexes [4]. Most of these hydrocyanation reactions utilize highly volatile, toxic and expensive hydrogen cyanide or trimethylsilyl cyanide (TMSCN) as a source of cyanide to achieve cyanohydrins or *O*-trimethylsilyl cyanohydrins, respectively at a very low temperature. Although less expensive cyanide sources, such as ethyl cyano formate, and benzoyl cyanide, have been used to achieve *O*-protected cyanohydrins [5–11], exploring an inexpensive and non-volatile source of cyanide under milder reaction conditions is still interesting.

In recent years, Belokon et al. have reported some very efficient catalysts based on Ti(IV) and V(V)=O complexes for asymmetric *O*-acetylcyanation of aldehydes using potassium cyanide as a cyanide source to give desired cyanohydrin with ee up to 92% at –42 °C [12]. As chiral catalysts are expensive their recycling is necessary for their commercial exploitation. Recently, many efforts have been made to develop recyclable metal complexes using organic or inorganic supports [13] and ionic liquids [14] but these methods demand major modification in the structure of the catalysts.

We have an ongoing interest in the design and development of recyclable dimeric/polymeric salen complexes [15] as catalysts for various asymmetric organic transformations, herein, we are extending the application of recyclable polymeric salen ligand [15c] for asymmetric *O*-acetyl cyanation of various aromatic aldehydes. The polymeric salen ligand was used to synthesize its vanadium(V) complex **1** that was applied as catalyst with potassium cyanide as an inexpensive and non-volatile source of cyanide to various aldehydes in the presence of acetic anhydride at –20 °C. Quantitative yield (99%) of *O*-acetylcyanohydrins with high chiral induction (ee, up to 96%) was achieved in the case of 2-methylbenzaldehyde. Besides, we have observed that the V(V) salen complex is an efficient recyclable catalyst in term of reactivity and enantioselectivity with added advantages of recyclability.

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2. Experimental

2.1. Materials and methods

Vanadyl sulphate hydrate (Loba Chemie, India), benzaldehyde, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, 2-methoxybenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-fluorobenzaldehyde, valeraldehyde (Aldrich), 2-methylbenzaldehyde, 4-methylbenzaldehyde, KCN were purchased from Merck Chemicals and were used as received. All the solvents were dried by standard procedures [16], distilled and stored under nitrogen. The synthesis and characterization of poly[(*R,R*)-*N,N'*-bis-{3-(1,1-dimethylethyl)-5-methylene salicylidene} cyclohexane-1,2-diamine] **1'** and its precursors was carried out as described in Ref. [15c].

2.2. Instrumentation

Microanalysis of the complex was done on CHNS analyzer, Perkin-Elmer model 2400. NMR spectra were obtained with a Bruker F113V spectrometer (200 MHz and 50 MHz for ^1H and ^{13}C , respectively) and are referenced internally with TMS. FTIR spectra were recorded on Perkin-Elmer Spectrum GX spectrophotometer in KBr window. High-resolution mass spectra were obtained with a LC-MS (Q-TOF) LC (Waters), MS (Micromass) instruments. For the product purification, flash chromatography was performed using silica gel 60–200 mesh purchased from s.d. Fine-Chemicals Limited, Mumbai (India). The conversions of *O*-acetylcyanohydrin were determined by capillary GC column SPB-5 (60 m) using Shimadzu 2010 with respect to internal standard (*n*-tridecane). Enantiomeric excess (ee) were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chiralpak OD and AD chiral columns with 2-propanol/hexane as eluent. HPLC traces were compared to racemic samples. Optical rotations were measured with a Digipol 781 Automatic Polarimeter, Rudolph Instrument. An inductively coupled plasma spectrometer (Perkin-Elmer, USA; modal ICP Optima 3300 RL) was used for V estimation.

2.2.1. Synthesis of polymeric vanadium(V) complex **1**

The ligand **1'** (0.799 g, 1.79 mmol) was dissolved in mixed solvent ethanol: CH_2Cl_2 (3:2, 15 ml) to which an aqueous solution of vanadyl sulphate hydrate (0.453 g, 1.79 mmol in 2 ml water) was added dropwise under an inert atmosphere at RT. The resulting solution was refluxed for 4 h and then cooled to room temperature with an extended stirring for 12 h while opening the side arm of the reaction flask. Solvent was completely evaporated and the residue was dissolved in CH_2Cl_2 (10 ml), washed with water (3 ml \times 5 ml) and finally with brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered and evaporated to give polymeric V(V) complex. Yield, 0.680 g, 73.9%; mp: 204–210 °C; IR: (KBr) $\bar{\nu}$ = 3473, 2957, 2867, 1612, 1536, 1466, 1387, 1345, 1315, 1216, 1177, 1030, 987, 887, 821, 789, 748, 714, 662, 567 cm^{-1} ; $[\alpha]_{\text{D}}^{30}$ = –204.61 (c = 0.05, CH_2Cl_2); $\lambda_{\text{max}}(\epsilon)$: 236 (45,090), 404 (11,680), 630 (2620); ^1H NMR (200 MHz, CDCl_3): δ 0.85 (t, J = 7.2, 3H), 1.30 (s, 18H), 1.51–1.88 (m, 8H), 3.31 (q, J = 7.2, 2H), 3.39 (s, 2H), 4.26 (m,

2H), 6.89–7.24 (m, 4H), 8.26 (bs, 2H) ppm; ^{13}C NMR (50 MHz, CDCl_3): δ 13.4, 23.4, 26.2, 28.9, 30.0, 40.8, 63.6, 121.3, 128.2, 132.0, 135.6, 160.6, 168.3; anal. calcd for $\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_8\text{SV}$: C, 56.88; H, 6.57; N, 4.28. Found: C, 56.92; H, 6.58; N, 4.30.

2.2.2. Procedure for vanadium(V) polymeric salen-catalyzed asymmetric *O*-acetylcyanation of aldehydes

V(V)-polymeric salen catalyst **1** (0.050 g, 0.099 mmol) (with respect to single salen unit) was dissolved in dry CH_2Cl_2 (3 ml) and the solution was cooled to –20 °C. Dry CH_2Cl_2 (2 ml), *t*-BuOH (0.2 ml, 2 mmol), H_2O (20 μl , 1.1 mmol), appropriate aldehyde **2a–i** (1.98 mmol) and Ac_2O (0.748 ml, 7.92 mmol) were then added to the solution in that order. The addition of KCN (0.515 g, 7.92 mmol) was done slowly during 2 h followed by the addition of dry CH_2Cl_2 (3 ml). After the reaction was completed (as detected by TLC), the reaction mass was washed with water (3 ml \times 5 ml) followed by brine, the organic layer was separated, and dried over anhydrous Na_2SO_4 . The solution was filtered, evaporated and compound was purified by flash column chromatography on silica gel (eluted with hexane/ethylacetate = 95:5). The enantiomeric excess of the product *O*-acetylcyanohydrins was determined by HPLC using Chiralpak OD and AD column.

2.2.3. Recycling of the catalyst

The polymeric V(V) salen complex **1**, has inherent property to get precipitated in hexane. Therefore, after the completion of reaction (detected by TLC), hexane (5 ml) was added into the reaction solution, stirred for 15 min and then filtered, the filtrate was analyzed by GC and the catalyst was precipitated, washed with distilled water thoroughly, followed by hexane (15 ml), dried in vacuo and reused for the subsequent runs.

2.2.4. Spectroscopic data for product **3a–h**

2.2.4.1. (*S*)-2-*O*-Acetyl-2-phenyl acetonitrile (**3a**). ^1H NMR (200 MHz, CDCl_3): δ 2.11 (s, 3H), 6.38 (s, 1H), 7.40–7.52 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3): δ 20.8, 63.3, 116.7, 128.3, 129.7, 130.8, 132.3, 169.4; $[\alpha]_{\text{D}}^{30}$ = –30.5 (c = 1, CH_2Cl_2); TOF-MS (ESI+): m/z 160.2 ($M+H$) $^+$; HPLC analysis: Chiralpak OD column, hexane/isopropanol = 99:1, flow rate 0.8 ml/min, R_{t1} = 18.60 min (minor), R_{t2} = 20.50 min (major).

2.2.4.2. (*S*)-2-*O*-Acetyl-2-(4-methoxyphenyl) acetonitrile (**3b**). ^1H NMR (200 MHz, CDCl_3): δ 2.14 (s, 3H), 3.83 (s, 3H), 6.35 (s, 1H), 6.92–6.97 (d, J = 8.75, 2H), 7.42–7.47 (d, J = 8.90, 2H); ^{13}C NMR (50 MHz, CDCl_3): δ 21.14, 56.09, 63.26, 115.07, 115.26, 130.30, 132.64, 161.85, 169.66; $[\alpha]_{\text{D}}^{30}$ = –24.15 (c = 1, CH_2Cl_2); TOF-MS (ESI+): m/z 207.18 ($M+H$) $^+$; HPLC analysis: Chiralpak OD column, hexane/isopropanol = 99:1, flow rate 0.8 ml/min: R_{t1} = 27.95 min (minor), R_{t2} = 31.63 min (major).

2.2.4.3. (*S*)-2-*O*-Acetyl-2-(3-methoxyphenyl) acetonitrile (**3c**). ^1H NMR (200 MHz, CDCl_3): δ 2.16 (s, 3H), 3.83 (s, 3H), 6.37 (s, 1H), 6.96–7.39 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3): 21.00, 56.02, 63.33, 113.91, 116.61, 120.54, 130.95, 133.72, 160.77, 169.45; $[\alpha]_{\text{D}}^{30}$ = –23.12 (c = 1, CH_2Cl_2); TOF-MS (ESI+): m/z

207.38 ($M+H$)⁺; HPLC analysis: Chiralpak OD column, hexane/isopropanol=99:1, flow rate 0.8 ml/min: R_{t1} = 27.00 min (minor), R_{t2} = 34.47 min (major).

2.2.4.4. (*S*)-2-*O*-Acetyl-2-(2-methoxyphenyl) acetonitrile (**3d**). ¹H NMR (200 MHz, CDCl₃): δ 2.13 (s, 3H), 3.85 (s, 3H), 6.68 (s, 1H), 6.91–7.57 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 20.82, 56.23, 68.58, 111.68, 116.75, 121.15, 129.15, 132.29, 157.25, 169.34; [α]_D³⁰ = −25.61 (c = 1, CH₂Cl₂); TOF-MS (ESI⁺): m/z 207.14 ($M+H$)⁺; HPLC analysis: Chiralpak OD column, hexane/isopropanol=99:1, flow rate 0.8 ml/min, R_{t1} = 19.86 min (major), R_{t2} = 22.80 min (minor).

2.2.4.5. (*S*)-2-*O*-Acetyl-2-(4-cholophenyl) acetonitrile (**3e**). ¹H NMR (200 MHz, CDCl₃): δ 2.15 (s, 3H), 6.25 (s, 1H), 7.37–7.42 (d, J = 8.70, 2H), 7.44–7.49 (d, J = 8.56, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 20.78, 62.62, 116.70, 129.69, 129.89, 130.86, 132.87, 169.23; [α]_D³⁰ = −12.20 (c = 1, CH₂Cl₂); TOF-MS (ESI⁺): m/z 211.20 ($M+H$)⁺; HPLC analysis: Chiralpak OD column, hexane/isopropanol = 99:1, flow rate 0.8 ml/min, R_{t1} = 26.93 min (minor), R_{t2} = 30.13 min (major).

2.2.4.6. (*S*)-2-*O*-Acetyl-2-(4-bromophenyl) acetonitrile (**3f**). ¹H NMR (200 MHz, CDCl₃): δ 2.16 (s, 3H), 6.36 (s, 1H), 7.32–7.41 (d, J = 8.52, 2H), 7.56–7.60 (d, J = 8.38, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 20.98, 62.84, 116.31, 125.45, 129.42, 130.99, 133.12, 169.29; [α]_D³⁰ = −13.36 (c = 1, CH₂Cl₂); TOF-MS (ESI⁺): m/z 153.10 ($M+H$)⁺; HPLC analysis: Chiralpak OD column, hexane/isopropanol = 99:1, flow rate 0.8 ml/min, R_{t1} = 32.99 min (minor), R_{t2} = 37.70 min (major).

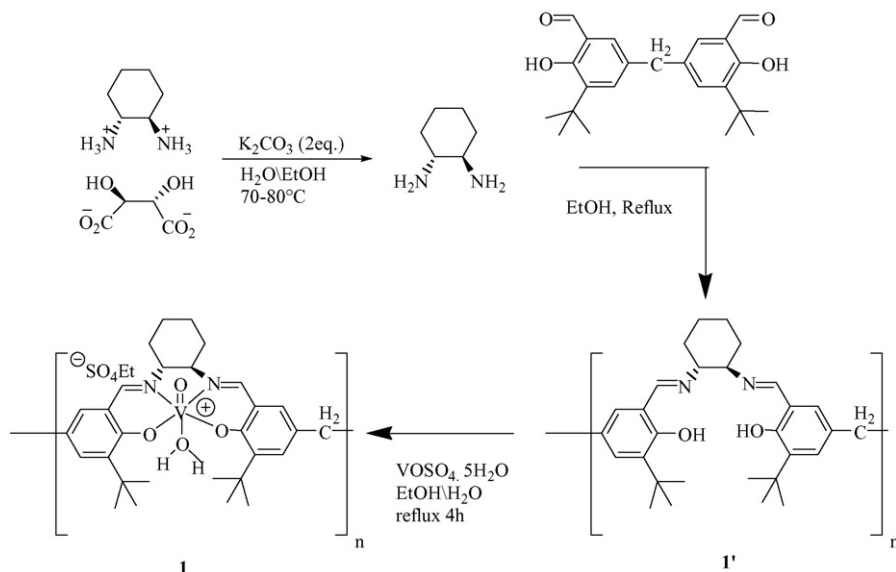
2.2.4.7. (*S*)-2-*O*-Acetyl-2-(4-fluorophenyl) acetonitrile (**3g**). ¹H NMR (200 MHz, CDCl₃): δ 2.16 (s, 3H), 6.39 (s, 1H), 7.09–7.18 (m, 2H), 7.49–7.55 (m, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 21.01, 68.79, 116.72, 117.22, 129.43, 130.62, 160.89, 169.45; [α]_D³⁰ = −21.28 (c = 1, CH₂Cl₂); TOF-MS (ESI⁺): m/z

195.19 ($M+H$); HPLC analysis: Chiralpak AD column, hexane/isopropanol=99:1, flow rate 0.8 ml/min, R_{t1} = 20.93 min (minor), R_{t2} = 22.68 min (major).

2.2.4.8. (*S*)-2-*O*-Acetyl-2-(2-methylphenyl) acetonitrile (**3h**). ¹H NMR (200 MHz, CDCl₃): δ 2.17 (s, 3H), 2.43 (s, 3H), 6.51 (s, 1H), 7.23–7.58 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 21.02, 19.56, 61.68, 113.19, 127.47, 129.23, 130.82, 131.16, 131.99, 138.22, 169.03; [α]_D³⁰ = −26.22 (c = 1, CH₂Cl₂); TOF-MS (ESI⁺): m/z 191.03 ($M+H$)⁺; HPLC analysis: Chiralpak AD column, hexane/isopropanol = 99:1, flow rate 0.8 ml/min, R_{t1} = 16.49 min (major), R_{t2} = 20.07 min (minor).

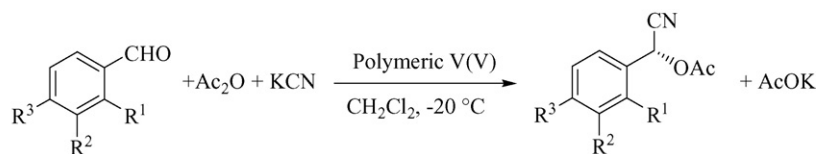
3. Results and discussion

Polymeric V(V) salen complex **1** was synthesized by condensation of mono tartrate salt of 1*R*,2*R*-(−)-diaminocyclohexane with 5,5′-methylene-bis(3-*tert*-butyl salicylaldehyde) in equimolar ratio in methanol to get polymeric salen ligand, which was eventually reacted with vanadyl sulphate hydrate as depicted in Scheme 1. ¹H NMR and IR showed the absence of aldehyde group in the ligand **1'**. The number of repetitive units and average molecular weight of the polymeric ligand as measured by vapour pressure osmometry was ~5400 (n = 12). Vanadium content in complex **1** was found to be 9.36 ppm (c = 0.0191 mmol complex in 100 ml H₂O) by ICP analysis. The complex **1** was used as an active catalyst for the asymmetric addition of potassium cyanide in the presence of acetic anhydride at −20 °C to various aldehydes viz., benzaldehyde (**2a**), 4-methoxybenzaldehyde (**2b**), 3-methoxybenzaldehyde (**2c**), 2-methoxybenzaldehyde (**2d**), 4-chlorobenzaldehyde (**2e**), 4-bromobenzaldehyde (**2f**), 4-fluorobenzaldehyde (**2g**), 2-methylbenzaldehyde (**2h**), 4-methylbenzaldehyde (**2i**) and data are given in Table 1. Initially catalytic reaction was performed with benzaldehyde as a model substrate using KCN as a source of cyanide that gave exclu-



Scheme 1. Synthesis of the complex **1**.

Table 1

Enantioselective synthesis of the *O*-acetylcyanohydrin from various aldehydes, potassium cyanide and acetic anhydride catalyzed by polymeric V(V) complex**2a**; R¹ = H, R² = H, R³ = H**2b**; R¹, R² = H, R³ = OMe**2c**; R¹ = H, R² = OMe, R³ = H**2d**; R¹ = OMe, R² = H, R³ = H**2e**; R¹ = H, R² = H, R³ = Cl**2f**; R¹ = H, R² = H, R³ = Br**2g**; R¹ = H, R² = H, R³ = F**2h**; R¹ = Me, R² = H, R³ = H**2i**; R¹ = H, R² = H, R³ = Me**3a-i**

Entry	Substrate	Time (h)	Conversion (%) ^a	ee (%) ^b	TOF (h ⁻¹) ^c	Confign.
1	2a	9	95	91	2.11	<i>S</i>
2	2b	9	90	82	2.00	<i>S</i>
3	2c	9	91	89	2.02	<i>S</i>
4	2d	9	91	88	2.02	<i>S</i>
5	2e	9	98	90	2.17	<i>S</i>
6	2f	9	99	89	2.20	<i>S</i>
7	2g	9	98	92	2.17	<i>S</i>
8	2h	9	99	96	2.20	<i>S</i>
9	2i	9	96	93	2.13	<i>S</i>

All reactions carried out at -20°C .^a The conversion of *O*-acetylcyanohydrin was determined based on GC integral area.^b The ee was determined by using Chiralpak HPLC OD and AD column and compared with literature [12b].^c TOF = [product]/[catalyst] × time (h⁻¹) TOF is based on monomeric salen unit.

sively the product **3a** as confirmed by ¹H and ¹³C NMR with no trace of enolizable cyanohydrin (data given in Section 2). It is evident from the table that the present catalytic protocol is quite general for a range of substrates used in the present study. However, the substituents on benzaldehyde derivative had some influence on the reactivity and enantioselectivity. Excellent conversions to *O*-acetylcyanohydrin (95–99%) (Table 1, entries 1, 5–9) were obtained for most of the aldehydes in 9 h as shown by the turn over frequency (TOF) values. However, methoxy substituted aldehydes (Table 1, entries 2–4) have shown relatively lesser conversions to *O*-acetylcyanohydrin (90%). The lower conversions for 4-methoxy benzaldehyde has also been reported with dimeric/non-recyclable polymeric V(V) salen complexes [4d, 15b]. On carrying out the cyanation reaction with aliphatic aldehyde such as valeraldehyde in the presence of KCN and acetic anhydride at -20°C , 90% conversion with 90% ee of *O*-acetylcyanohydrin was achieved in 9 h.

In order to compare the reactivity of monomeric V(V) complex and polymeric V(V) salen complex **1**, we have conducted the kinetic reaction for cyanation of benzaldehyde as representative substrate using KCN as source of cyanide at -20°C . At the beginning of cyanation reaction, the kinetic runs found to be fast (Fig. 1). The initial rate constant k_{obs} were determined by directly estimating the amount of *O*-acetylcyanohydrin formed up to completion of the reaction which gave the k_{obs} value $106.9 \times 10^{-3} \text{ M/h}$ for complex **1** while for monomeric V(V)

complex this value was found to be $55.5 \times 10^{-3} \text{ M/h}$ suggesting that in polymeric V(V) the active catalytic sites do not operate in isolation but interact.

The choice of solvent has a significant effect on the reactivity and enantioselectivity of *O*-acetylcyanohydrin formation using chiral metal salen complexes [4d]. Therefore, we studied

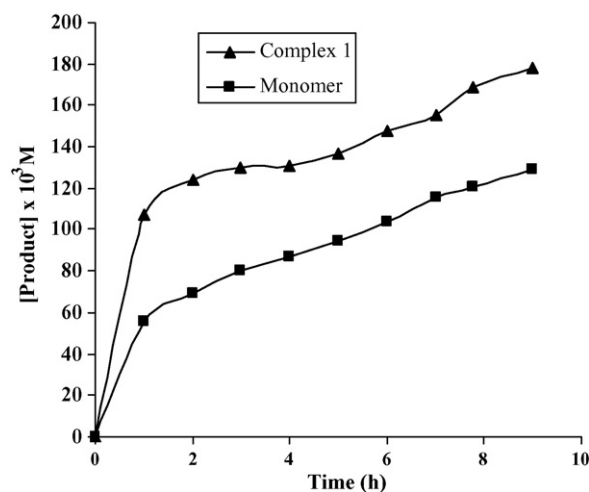


Fig. 1. Time dependent plot of the formation of *O*-acetylcyanohydrin at -20°C , [catalyst **1**] = $7.6 \times 10^{-3} \text{ M}$, [benzaldehyde] = $198.1 \times 10^{-3} \text{ M}$, [KCN] = $789.4 \times 10^{-3} \text{ M}$.

Table 2

Data for the effect of solvents on conversion and ee of *O*-acetylcyanohydrin using benzaldehyde as representative substrate with catalysts **1** using KCN as cyanide source

Entry	Solvent	Conversion (%) ^a	ee (%) ^b
10	Dichloromethane	95	91
11	1,2-Dichloroethane	80	75
12	Toluene	55	72
13	Tetrahydrofuran	60	65

^a The conversion of *O*-acetylcyanohydrin was determined based on GC integral area.

^b The ee was determined by Chiralpak HPLC OD column and compared with literature [12b].

the effect of various solvents in asymmetric addition of KCN and acetic anhydride to benzaldehyde as representative substrate using the complex **1** and results are shown in Table 2. Good conversion (80%) and ee (75%) (Table 2, entry 11) was achieved when 1,2-dichloroethane was used as solvent while in the case of toluene and THF the conversion (55–60%) and enantioselectivity (ee, 65–72) (Table 2, entries 12, 13) were lower. Of all the solvents used dichloromethane was found to be the solvent of choice (entry 10) and it showed better results than the previously reported other chiral polymeric salen complex with V(V) [4d].

The literature shows that catalyst loading and temperature variation have pronounced effect on the reactivity and enantioselectivity in asymmetric cyanation reactions [4d]. Hence, the complex **1** was used for examining the influence of catalyst loading and temperature variation on the formation of *O*-acetylcyanohydrin using benzaldehyde as a representative substrate and KCN as cyanide source. The data given in Table 3 shows excellent conversion (95%) and ee (91%) at –20 °C with 5 mol% (with respect to single salen unit) of the complex **1** (Table 3, entry 14). On reducing the catalyst loading from 5 mol% to 2 mol% there is decrease in conversion 90% (Table 3, entry 15) with retention in ee 90%. On further decreasing the catalyst loading (1 mol%) there was drastic decrease in conversion and ee (entry 16). Furthermore, on increasing the reaction temperature of the catalytic run the yield and enantioselectivity of the product is adversely effected (entries 17–19). These observations are in agreement with earlier report [4d].

Table 3

Data for the effect of catalyst loading and reaction temperature on the conversion and ee of *O*-acetylcyanohydrin using benzaldehyde as representative substrate with catalyst **1** using KCN as cyanide source

Entry	Catalyst loading (mol%)	Temperature (°C)	Conversion (%) ^a	ee (%) ^b
14	5	–20	95	91
15	2	–20	90	90
16	1	–20	50	51
17	5	0	93	69
18	5	RT	90	65
19	5	–10	90	75

^a The conversion of *O*-acetylcyanohydrin was determined based on GC integral area.

^b The ee was determined by Chiralpak HPLC OD column and compared with literature [12b].

Table 4

Data for enantioselective synthesis of the *O*-acetylcyanohydrin with benzaldehyde, KCN and acetic anhydride catalyzed by recovered polymeric chiral V(V) complex

Run	1	2	3	4	5
Time (h)	9	9	9	9	9
Conversion (%) ^a	95	90	88	86	84
ee (%) ^b	91	91	91	91	91

All reaction carried out at –20 °C.

^a The conversion of *O*-acetylcyanohydrin was determined based on GC integral area.

^b The ee was determined by Chiralpak HPLC OD column and compared with literature [12b].

The recovered catalyst **1** was reused by adding fresh substrates and reactants in the similar manner as in the case with fresh catalyst. After each use the catalyst was precipitated by the addition of hexane to the reaction mixture, the precipitated catalyst was dried in vacuum and was used without further purification. The data of four-time use of the same catalyst is given in Table 4. The activity of the recycled catalysts gradually decreased upon successive use possibly due to some physical loss of the catalyst as loss of enantioselectivity was not observed in reuse experiments. The recyclability of this catalytic system has clear edge over previously reported polymeric V(V) salen complexes [4d].

4. Conclusion

In conclusion we have developed new recyclable polymeric vanadium(V) salen complex as efficient catalyst for the asymmetric addition of potassium cyanide to various aldehydes in the presence of acetic anhydride at –20 °C. The system turned out to be an efficient recyclable system in term of reactivity and enantioselectivity. The catalyst was recovered after first use and recycled four times with retention of enantioselectivity.

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References

- [1] (a) H. Griengl, A. Hickel, D.V. Johnson, C. Kratky, M. Schmidt, H. Schwab, *J. Chem. Soc., Chem. Commun.* (1997) 1933; (b) M. Schmidt, H. Griengl, *Top. Curr. Chem.* 200 (1999) 193.
- [2] (a) J.-I. Oku, S. Inoue, *J. Chem. Soc., Chem. Commun.* (1981) 229; (b) A. Mori, Y. Ikeda, K. Kinoshita, S. Inoue, *Chem. Lett.* (1989) 2119.
- [3] J.M. Brunel, I.P. Holmes, *Angew. Chem. Int. Ed.* 43 (2004) 2752.
- [4] (a) M. Hayashi, Y. Miyamoto, T. Inoue, N. Oguni, *J. Org. Chem.* 58 (1993) 1515; (b) Y.N. Belokon, S. Caveda-Cepas, B. Green, N.S. Ikonnikov, V.N. Khrustalev, V.S. Larichev, M.A. Moskalenko, M. North, C. Orizu, V.I.M. Tararov, G.I. Tasinazzo, L. Timofeeva, V. Yashkina, *J. Am. Chem. Soc.* 121 (1999) 3968;

- (c) X. Zhou, G.J.-S. Huang, P.-H. Ko, K.-K. Cheng, C.-M. Che, *J. Chem. Soc., Dalton Trans.* (1999) 3303;
- (d) W. Huang, Y. Song, J. Wang, G. Cao, Z. Zheng, *Tetrahedron* 60 (2004) 10469.
- [5] Y.N. Belokon, A.J. Blacker, L.A. Clutterbuck, M. North, *Org. Lett.* 5 (2003) 4505.
- [6] J. Casas, A. Baeza, J.M. Sansano, C. Najera, J.M. Saa, *Tetrahedron: Asymmetry* 14 (2003) 197.
- [7] J. Tian, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Org. Lett.* 5 (2003) 3021.
- [8] J. Tian, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Angew. Chem. Int. Ed.* 41 (2002) 3636.
- [9] S.K. Tian, L.A. Deng, *J. Am. Chem. Soc.* 123 (2001) 6195.
- [10] D.A. Nicewicz, C.M. Yates, J.S. Johnson, *Angew. Chem. Int. Ed.* 43 (2004) 2652.
- [11] T. Watahiki, S. Ohba, T. Oriyama, *Org. Lett.* 5 (2003) 2679.
- [12] (a) Y.N. Belokon, A.V. Gutnov, M.A. Moskalenko, L.V. Yashkina, D.E. Lesovoy, N.S. Ikonnikov, V.S. Larichev, M. North, *J. Chem. Soc., Chem. Commun.* (2002) 244;
- (b) Y.N. Belokon, P. Carta, A.V. Gutnov, V. Maleev, M.A. Moskalenko, L.V. Yashkina, N.S. Ikonniko, N.V. Voskoboev, V.N. Khrustalev, M. North, *Helvetica Chim. Acta* 85 (2002) 3301;
- (c) Y.N. Belokon, B. Green, N.S. Ikonnikov, M. North, T. Parsons, V.I. Tararov, *Tetrahedron* 57 (2001) 771;
- (d) Y.N. Belokon, B. Green, N.S. Ikonnikov, V.S. Larichev, B.V. Lokshin, M.A. Moskalenko, M. North, C. Orizu, A.S. Peregudov, G.I. Timofeeva, *Eur. J. Org. Chem.* (2000) 2655;
- (e) Y.N. Belokon, A.J. Blacker, P. Carta, L.A. Clutterbuck, M. North, *Tetrahedron* 60 (2004) 10433.
- [13] (a) C. Baleizão, B. Gigante, H. Garcia, A. Corma, *J. Catal.* 215 (2003) 199;
- (b) C. Baleizão, B. Gigante, H. Garcia, A. Corma, *Tetrahedron* 60 (2004) 10461.
- [14] (a) C. Baleizão, B. Gigante, H. Garcia, A. Corma, *Green Chem.* 4 (2002) 272;
- (b) C. Baleizão, B. Gigante, H. Garcia, A. Corma, *Tetrahedron Lett.* 44 (2003) 6813.
- [15] (a) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, R.V. Jasra, *Tetrahedron: Asymmetry* 12 (2001) 433;
- (b) N.H. Khan, S. Agrawal, R.I. Kureshy, S.H.R. Abdi, V.J. Mayani, R.V. Jasra, *Eur. J. Org. Chem.* (2006) 3175;
- (c) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S. Singh, I. Ahmad, R.V. Jasra, *J. Mol. Catal.* 218 (2004) 141;
- (d) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, R.V. Jasra, *J. Mol. Catal.* 179 (2002) 73;
- (e) R.I. Kureshy, S. Singh, N.H. Khan, S.H.R. Abdi, S. Agrawal, R.V. Jasra, *Tetrahedron: Asymmetry* 17 (2006) 1638.
- [16] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1981.